The characterization of volatile matter in charcoal and its implications for soil fertility

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Terra Preta do Indio

Photo source: University of Bayreuth

Terra Preta Soil

Typical Upland Amazonian Soil
“Terra Preta Novo” : Charcoal Vision

Plant response to charcoal additions

- With no charcoal additions
- With 20% (w/w) charcoal addition
# Differential effect on plant growth

<table>
<thead>
<tr>
<th>Study</th>
<th>Charcoal feedstock</th>
<th>Production Temp</th>
<th>Crop</th>
<th>Rate</th>
<th>Positive effect on biomass</th>
<th>Negative effect on biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lehmann et al., 2002</td>
<td>secondary forest</td>
<td>?</td>
<td>Cowpea</td>
<td>10%</td>
<td>almost 50% increase</td>
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<tr>
<td>Chan et al., 2007</td>
<td>greenwaste</td>
<td>450°C</td>
<td>Radish</td>
<td>2%</td>
<td>50% decrease</td>
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<tr>
<td>Chan et al., 2008</td>
<td>poultry</td>
<td>450°C</td>
<td>Radish</td>
<td>2%</td>
<td>30% increase</td>
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<tr>
<td>Chan et al., 2009</td>
<td>poultry</td>
<td>550°C</td>
<td>Radish</td>
<td>2%</td>
<td>almost 50% increase</td>
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<tr>
<td>Gundale and De Luca, 2007</td>
<td>wildfire</td>
<td>High temp</td>
<td><em>K. Macrantha</em></td>
<td>2%</td>
<td>120% increase</td>
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<td>Gundale and De Luca, 2007</td>
<td>Douglas-fir</td>
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<td><em>K. Macrantha</em></td>
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<td>36% decrease</td>
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<tr>
<td>Gundale and De Luca, 2007</td>
<td>ponderosa pine</td>
<td>350°C</td>
<td><em>K. Macrantha</em></td>
<td>2%</td>
<td>25% decrease</td>
<td></td>
</tr>
</tbody>
</table>

Effects of charcoal production temperature
Spectrum of Charred Materials

- **Volatile Matter (VM) content**: a measure of the susceptibility of charcoal (char) to further decompose and form carbon when heated

63% VM Content

More thermally altered

7% VM Content
Inverse relationship to carbonization temperature

- **<250°C**
  - Simple sugars are preserved
  - Appearance of aromatic carbon compounds
  - High VM

- **250 - 300°C**
  - Condensed carbon compounds with loss of oxygen and hydrogen

- **300 - 450°C**
  - Formation of condensed carbon compounds
  - Low VM

- **450 - 650°C**
  - Further carbonization
## Effect of VM content on plant growth

<table>
<thead>
<tr>
<th>Study</th>
<th>Charcoal feedstock</th>
<th>Production Temp</th>
<th>Crop</th>
<th>Rate</th>
<th>Positive effect on biomass</th>
<th>Negative effect on biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rondon et al., 2007</td>
<td>Eucalyptus</td>
<td>350°C, 33% VM</td>
<td>Common bean non-N fixer</td>
<td>10%</td>
<td>15% decrease</td>
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<tr>
<td>Rondon et al., 2007</td>
<td>Eucalyptus</td>
<td>350°C, 33% VM</td>
<td>Common bean-N fixer</td>
<td>10%</td>
<td>no effect</td>
<td>no effect</td>
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<tr>
<td>Deenik et al., 2010</td>
<td>macadamia nutshell</td>
<td>22.5% VM</td>
<td>Lettuce</td>
<td>5%</td>
<td>no effect</td>
<td>no effect</td>
</tr>
<tr>
<td>Deenik et al., 2010</td>
<td>macadamia nutshell</td>
<td>22.5% VM</td>
<td>Lettuce</td>
<td>10%</td>
<td>20% decrease</td>
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<tr>
<td>Deenik et al., 2010</td>
<td>macadamia nutshell</td>
<td>22.5% VM</td>
<td>Lettuce</td>
<td>20%</td>
<td>70% decrease</td>
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<tr>
<td>Deenik et al., 2010</td>
<td>macadamia nutshell</td>
<td>22.5% VM</td>
<td>Corn</td>
<td>10%</td>
<td>50% decrease</td>
<td></td>
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<tr>
<td>Deenik et al., 2010</td>
<td>macadamia nutshell</td>
<td>6.3% VM</td>
<td>Corn</td>
<td>10%</td>
<td>15% increase</td>
<td></td>
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</tbody>
</table>

*Nitrogen deficiencies*
As a soil amendment
Research Goals

- To characterize the VM content in charcoal, in order to improve our understanding the effect of different charcoals on soil fertility
  - Microbial and nitrogen dynamics
  - Nutrient holding capacity

- To improve our predictions of how plants and microbes respond to soils amended with various charcoal types.
Studies

1. Charcoal characterization

2. Effect of VM content in charcoal on soil microbial and nitrogen dynamics

3. Effect of fresh and aged charcoals on soil charge characteristics (e.g. cation exchange capacity)
Study #1: Characterization

Objectives:
1. To characterize charcoals with different VM contents and feedstocks
2. To relate differences in structure and extractable molecular compounds to charcoal behavior in soil

Hypotheses:
• The VM content = phenolic compounds and hydrocarbons
• These compounds are presumably bioavailable and could potentially inhibit plant growth in the short term
Procedures for Study #1

Charcoal Types
1. 63% VM corncob  
2. 23% VM corncob  
3. 7% VM corncob  
4. 23% VM kiawe  
5. Commercial activated charcoal  
6. 23% VM corncob extracted with acetone

4 Techniques
1. Fourier transformed infrared spectroscopy (FTIR)  
2. Nuclear magnetic resonance (NMR)  
3. Gas chromatography mass spectroscopy (GC-MS)  
4. Prussian Blue for Total Phenols
Fractionation of charcoal

Fresh, original charcoal

Acetone

Extracted Charcoal

Extractable materials from the charcoal

105°C
Chemical structure—NMR and FTIR

Fresh, original charcoal

Extractable materials from the charcoal

FTIR and NMR
1. FTIR—chemical structure

**Activated Charcoal**
- OH of carboxyl carbon

**7% VM corncob**
- OH of carboxyl C
- C=O stretching
- C=C aromatic C
- C=O stretching
- weak CH₂ stretch vibrations of aliphatic carbon

**23% VM kiawe**
- CH deformation of aliphatic carbon
- OH stretching vibrations of H-bonded hydroxyl groups of phenols

**23% VM corncob**
- CH₂ bending
- OH stretching vibrations of H-bonded hydroxyl groups of phenols
- CH deformation of aliphatic carbon

**Absorbance (arbitrary units)**

Wavenumbers (cm⁻¹)
2. NMR—chemical structure

Alkyl and O-substituted Alkyl C

Corn cob charcoals

Kiawe charcoal
2. NMR
Hypothetical Structures

Flash Carbonization Biochar, High VM

Flash Carbonization Biochar, Low VM

Kiawe Char
Composition of extractable components

Fresh, original 23% VM Corncob charcoal

FTIR and NMR

Extractable materials from the charcoal

GC-MS and Prussian Blue
3. GC-MS—extractable compounds
Corncob feedstock

- a. Dodecyl acrylate
- b. Palmitic acid
- c. Oleic acid
3. GC-MS

63% VM corncob charcoal

- a. Ethyl phenol
- b. Ethyl guaiacol
- c. Vinyl guaiacol
- d. Syringol
- e. Vanillin
- f. Tridecanol
- g. Benzopyranone
- h. Dodecyl acrylate
- i. Methoxyphenol
- j. Palmitic acid
- k. Fluorathene
- l. Pyrene

23% VM corncob charcoal

- a. Myristic aldehyde
- b. Dimethylethylphenol
- c. Dodecyl acrylate
- d. Oleamide
- e. Propanoic acid
3. GC-MS

7% VM corncob charcoal  Extracted 23% VM corncob

Chromatogram Plot
File: c:\varianws\data\jonathan\92109lvm.xms
Sample: 92109LVM  Operator: sc
Scan Range: 1 - 5722 Time Range: 5.12 - 46.51 min.

RIC Merged 92109lvm.xms  1200 CENTROID RAW
(+) EI Q1MS 40.0 - 550.0 >
Seg 1, Time: 5.12-46.51, Channels: 1
666 2036 3425 4820 Scans

Chromatogram Plot
File: c:\varianws\data\jonathan\92209ae.xms
Sample: 92209AE  Operator: sc
Scan Range: 1 - 5694 Time Range: 5.12 - 46.51 min.

RIC Merged 92209ae.xms  1200 CENTROID RAW
(+) EI Q1MS 40.0 - 550.0 >
Seg 1, Time: 5.12-46.51, Channels: 1
666 2035 3419 4802 Scans

7% VM corncob charcoal Extracted 23% VM corncob
3. GC-MS
Kiawe Feedstock and 23% VM Charcoal

Feedstock

23% VM kiawe char

- a. Dimethylethyl phenol
- b. Dodecyl acrylate
- c. Palmitic acid
- d. Oleic acid
- e. Stearic acid
- f. Octacosane
- g. Erucamide
- h. Lycopersene
- i. Nonacosane
- j. Vitamin E
- k. Campesterol
- l. Stigmasterol
- m. Alpha sitosterol
Prussian Blue for Total Phenols: Extracted with acetone

Total phenolics in charcoals

Charcoal type
- 23% VM cc
- 7% VM cc
- 23% kiawe
- 23% cc extracted

Microgram phenol/g charcoal

Charcoal type
- 23% VM cc
- 7% VM cc
- 23% kiawe
- 23% cc extracted
Measurable differences in the chemical structure and composition of charcoals

**VM content of charcoals** = mostly alkyl carbons and oxygen-substituted alkyl carbons (NMR), as well as phenolics (FTIR)

- GC-MS able to detect a range of extractable compounds that varied among chars, particularly feedstocks. Bioavailability?
  
  High VM corncob vs. High VM kiawe charcoal

- Unable to detect extractable compounds in kiawe char. What other types of chemical compounds makeup VM content? Py-GC-MS or HPLC?
Objective:
To determine the effect of VM content in charcoal on:
1. Soil microbial activity
2. Soil nitrogen dynamics

Hypotheses:
• A higher VM content will stimulate microbial growth and activity—resulting in N immobilization
• This effect will be attributed to the presence of bioavailable carbon compounds in high VM charcoal
Our previous greenhouse studies showed nitrogen deficiencies in plants amended with high VM charcoals.

High VM corncob charcoals contained hydrocarbons and an array of extractable molecular compounds.

Opportunity to determine the initial effects of VM content on microbial and nitrogen dynamics in a highly weathered subsoil.
One-month incubation—procedure

Soil: Leilehua subsoil

Charcoals
1. 34% VM corncob
2. 7% VM corncob

Nitrogen
1. 0 kg/ha
2. 150 kg/ha

Measurements
1. Water extractable organic carbon
2. Hydrolytic enzyme activity
3. Extractable ammonium and nitrate
Incubation 1: Organic carbon

Water extractable carbon

34% Volatile Matter Char

mg C kg⁻¹ soil

Day

Control

Low VM

High VM

Char
Incubation 1: Biological Activity

mg Fluorescein produced/g soil/3 hr

Ctrl
Ctrl+N
HVM
HVM+N
LVM
LVM+N

Volatile Matter + N

Volatile Matter

Other treatments
Incubation 1: Nitrogen

Extractable ammonium

mg NH₄/kg soil

Soil alone 34%
VM + N 34%
VM 34%

Incubation 1: Nitrogen

Soil + N
Soil + HVM char + N
We observed the stimulation of microbial activity and nitrogen immobilization in the one-month incubation by high VM corncob charcoal, as hypothesized.

A later greenhouse study showed that a high VM kiawe charcoal did not have a negative impact on plant growth.

- Remember GC-MS did not detect any carbon compounds

In a longer study, we aimed to compare the effects of corncob and kiawe charcoals with equivalent VM contents on microbial activity.

What if we leached the charcoal first with acetone? Same effect?
Two-month incubation—procedure

**Soil**: Leilehua subsoil

**Amendments**
1. Corncob feedstock
2. 7% VM corncob
3. 23% VM corncob
4. Kiawe feedstock
5. 23% VM kiawe
6. Extracted 23% VM corncob

**Nitrogen**: none added

**Measurements**
1. Hydrolytic enzyme activity
2. Extractable ammonium and nitrate
SEM micrographs of materials

- Corncob husks
- 23% VM corncob
- 7% VM corncob
- Kiawe feedstock
- 23% VM kiawe
Incubation 2: Biological Activity

FDA activity

Week 0 2 4 6 8 10
mg fluorescein/ g soil/3 hour
0
200
400
600
800
1000
1200
Control
corncob feedstock
kiawe feedstock
Incubation 2: Biological Activity

FDA activity

Week
0 2 4 6 8 10
mg fluorescein/ g soil/3 hour
-50
0
50
100
150
200
250
300
350
Control
HVM cc
LVM cc
HVM kiawe

23% VM kiawe
Soil alone
7% VM corncob
Fractions of 23% VM corncob char

Fresh, original 23% VM Corncob charcoal

Acetone

Extracted Charcoal

Extractable materials from the charcoal
Incubation 2: Biological Activity

Hydrolytic enzyme activity

23% VM corncob

Extracted 23% VM corncob

Soil alone
Incubation 2: Ammonium Nitrogen

Week
0 2 4 6 8 10
mg NH₄/kg soil
0 10 20 30 40
Control
corncob feedstock
kiawe feedstock

Corncob and Kiawe feedstocks
Soil alone
Incubation2: Nitrate nitrogen

![Graph showing nitrate nitrogen levels over weeks with different feedstocks]
Incubation 2: Ammonium Nitrogen

![Graph showing the effect of different char treatments on ammonium nitrogen over time.](image-url)

- **Control**
- **HVM cc**
- **LVM cc**
- **HVM kiawe**

**Soil alone**

- 23% VM corncob and kiawe chars

- 7% VM corncob

**Week**

0 2 4 6 8 10

**mg NH4/kg soil**

0 5 10 15 20 25 30 35 40
Incubation2: Nitrate nitrogen

Soil alone

7% VM corn cob

23% VM corn cob

23% VM kiawe

mg NO₃/ kg soil

week
23% corncob charcoals contained extractable compounds, detected by GC-MS

The removal of this fraction reduced its effect on microbial activity

Opportunity to determine the bioavailability of the extractable fraction of high VM corncob charcoal
  - Can the extractable carbon compounds support fungal growth and activity?
2-week incubation of inoculated charcoal and charcoal fractions

**Inoculum:** Charcoal fungus

**Fractions of 23% VM corncob char**
1. Original charcoal
2. Extracted charcoal
3. Extractable components

**Nutrition:** Fungal nutrient solution

**Measurements**
1. Fungal colony forming units
2. Hydrolytic enzyme activity
Fractions of 23% VM corncob charcoal

Fresh, original 23% VM Corncob charcoal

Extracted Charcoal

Extractable materials from the charcoal
Incubation 3: Fungal Growth and Activity

**Fungal counts and FDA activity**

- **Control**
- **Extracted Charcoal**
- **Original Charcoal**
- **Extractable materials**

![Graph showing fungal counts and FDA activity with error bars.](image-url)
High VM corncob chars stimulated greater microbial activity than low VM corncob.

High VM kiawe charcoal did **not** enhance microbial activity.

For a single feedstock, VM content provides information regarding its relative bioavailability. **BUT**

Characterization of charcoal's soluble chemical composition with GC-MS was a better predictor of the behavior of charcoal in soil.

Further research using more sensitive techniques for more complete molecular composition of VM content.
Study #3: Effect on Soil Charge

Objectives
1. To determine the effect of different charcoals on soil charge in aging experiments.
2. To relate findings to previous studies showing an enhancement of soil CEC.

Hypotheses
• Fresh charcoal exhibits variable charge and will enhance the soil’s CEC upon increasing oxidation.
• Charcoals with a higher VM content will undergo oxidation more rapidly.
Procedure for Study #3

Treatments
1. 23% VM corncob
   7% VM corncob
   23% VM kiawe
2. Halii Soil and Leilehua Soil
3. Incubated charcoal and charcoal/soil mixtures at 60°C

Charge Fingerprints
1. $\text{pH}_0$
2. Zero net point of charge (ZNPC)
3. Cation exchange capacity (CEC)
4. Anion exchange capacity (AEC)

Incubation with incremental measurements in time
Variable (pH dependent) soil charge

- **Variable charge**: negative or positive charge depending upon pH
- **At low pH**: protonation = positive charge
- **At high pH**: deprotonation = negative charge
- **pH₀**: pH where protonation = deprotonation
- **CEC**: total amounts of cations adsorbed onto the exchange sites
- **AEC**: the total amount of anions that are adsorbed to the exchange sites
- **Point of zero net charge (PZNC)**: pH for zero net charge in the entire soil system.
- **CEC = AEC**

![Graph showing pH and cmolc/kg relationship](image)

- **AEC**: adsorbed anions
- **CEC**: adsorbed cations
- **Zero Net Point of Charge (ZNPC)**
- **Protonation**: positive charge
- **Deprotonation**: negative charge
- **pH₀**: positive = negative
  Where there is only variable charge, pH₀ = ZNPC
1. Variable Charge of charcoals

![Diagram showing variable charge of charcoals](image)

- Fresh charcoal
- Aged charcoal

**pH₀**

**Net surface charge**

- 23% VM cc
- 7% VM cc
- 23% VM kiawe
Charcoals + Halii soil

<table>
<thead>
<tr>
<th>Charcoal</th>
<th>pH₀</th>
<th>ZNPC</th>
<th>CEC pH 7(cmol⁺ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7% VM corncob</td>
<td>5.2</td>
<td>5.53</td>
<td>3.49</td>
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<tr>
<td>23% VM corncob</td>
<td>5.09</td>
<td>5.79</td>
<td>3.23</td>
</tr>
<tr>
<td>23% VM kiawe</td>
<td>5.07</td>
<td>5.5</td>
<td>3.61</td>
</tr>
<tr>
<td>Halii soil</td>
<td>4.96</td>
<td>5.57</td>
<td>3.31</td>
</tr>
<tr>
<td>Fresh, Aged-10 wk</td>
<td>5.3</td>
<td>5.33</td>
<td>3.71</td>
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<tr>
<td>Fresh, Aged-10 wk</td>
<td>5.09</td>
<td>5.34</td>
<td>4.12</td>
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<tr>
<td>Fresh, Aged-10 wk</td>
<td>5.22</td>
<td>5.15</td>
<td>3.32</td>
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</table>
Charcoal/Leilehua Mixtures

Leilehua soil, 3 months

<table>
<thead>
<tr>
<th>Charcoal</th>
<th>pH₀ Fresh</th>
<th>pH₀ Aged-3 mo</th>
<th>ZNPC Fresh</th>
<th>ZNPC Aged-3 mo</th>
<th>CEC pH 7 (cmolₑ⁻ kg⁻¹) Fresh</th>
<th>CEC pH 7 (cmolₑ⁻ kg⁻¹) Aged-3 mo</th>
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<tr>
<td>7% VM corncob</td>
<td>4.38</td>
<td>4.23</td>
<td>4.21</td>
<td>3.9</td>
<td>9.83</td>
<td>8.31</td>
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<td>23% VM corncob</td>
<td>4.18</td>
<td>4.15</td>
<td>4.04</td>
<td>3.67</td>
<td>7.09</td>
<td>8.54</td>
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<td>23% VM kiawe</td>
<td>4.38</td>
<td>4.27</td>
<td>4.18</td>
<td>3.87</td>
<td>13.55</td>
<td>12.65</td>
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<tr>
<td>Soil alone</td>
<td>4.23</td>
<td>3.96</td>
<td>3.26</td>
<td>3.54</td>
<td>11.89</td>
<td>7.84</td>
</tr>
</tbody>
</table>
7% volatile matter corn cob charcoal

23% volatile matter corn cob charcoal

23% volatile matter kiawe charcoal
Aged High VM chars developed greater negative charge than the aged Low VM char
Shifts in ZNPC and pH₀ due to charcoal additions

But neither High VM nor Low VM chars dramatically increased soil CEC
  • Due to its variable charge? Masking effect?
  • How long before? At which rate could charcoal have a major increase CEC in soils of Hawaii?
Final Conclusions

- VM content is an informative but coarse measurement.
  - Good indicator of the degree of carbonization for one feedstock
  - But does not tell us a lot about bioavailability

- Extractable (soluble) fraction of charcoal provided important data regarding bioavailable carbon compounds.
  - Still need better technique to identify complete molecular composition of VM content

- High VM charcoals developed greater negative charge than the low VM charcoal.
- However, contrary to our hypothesis, no charcoal dramatically enhanced the soil’s CEC.
Charcoal Characteristic: Just the beginning
- Complexity of charcoal chemistry
- Taken an easily measured property and related its behavior (e.g. bioavailability in soil)—but with limitations

Soil CEC: Implications for Hawaii soils
- 70% clay=high specific surface
- Amending “like with like” (e.g. High specific surface, variable charged Hawaii soil with high specific surface, variable charged charcoal)
Acknowledgements

- Dr. Antal and the Hawaii Natural Energy Institute
  - Providing Flash Carbonized corn cob charcoal and proximate analyses
- Drs. Deenik, Uehara, Hue, Li for serving on my committee
- Bill Hockaday and Sonia Campbell for their expertise and technical contributions
- Drs. Yost and Habte for their guidance
- Aminata Diarra and Yudai Sumiyoshi for their assistance
- Puaonaona and Garvin, my lab mates
- CTAHR community and admin staff
### Charge summary

#### Halii Soil
- Charcoal extracts decreased the ZNPC versus control
- Charcoals had lesser ZNPC than control, except for week 5
- Charcoals had a greater pH₀ than control for all weeks
- Charcoals had a greater ZNPC than pH₀, expect for week 10 of kiawe charcoal
- LVM extracts had greater pH₀ than LVM char. HVM extracts had same pH₀ than HVM char. K extracts had slightly greater pH₀ than char.
- ZNPC for extracts was generally less than or equal to the charcoal ZNPC, except for LVM baseline, K baseline and K 10 week

#### Leilehua Soil
- HVM ZNPC more negative month 2 and 3. No change in pH₀
- LVM ZNPC more negative month 1, 2, 3. Slight decrease in pH₀
- Kiawe ZNPC more negative month 1, 2, 3. Slight decrease in pH₀
- Soil alone ZNPC slight increase month 1, 2, 3. Decrease in pH₀
- Charcoals always greater pH₀ than control throughout incubation (except HVM baseline)
- Charcoals always greater ZNPC than control, except HVM and LVM month 2
- Charcoals almost 1 pH unit greater ZNPC than control at baseline
## Halii Soil

<table>
<thead>
<tr>
<th></th>
<th>charcoal</th>
<th>charcoal/water extract</th>
<th>char-extract</th>
<th>pHo</th>
<th>ZNPC</th>
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<tbody>
<tr>
<td></td>
<td>HVM corncob</td>
<td>LVM corncob</td>
<td>HVM kiawe</td>
<td>Halii soil</td>
<td></td>
</tr>
<tr>
<td>pH₀</td>
<td>0.00 5 10</td>
<td>0.00 5 10</td>
<td>0.00 5 10</td>
<td>0.00 5 10</td>
<td></td>
</tr>
<tr>
<td>ZNPC</td>
<td>5.05 5.19 5.06</td>
<td>4.97 5.22 5.15</td>
<td>5.01 5.14 5.1</td>
<td>4.96</td>
<td></td>
</tr>
<tr>
<td>ZNPC-pH₀</td>
<td>0.71 0.36 0.25</td>
<td>0.25 1.01 0.18</td>
<td>0.12 0.63</td>
<td>-0.2</td>
<td>0.61</td>
</tr>
<tr>
<td>pH -ctrl</td>
<td>0.23 0.1 0.01</td>
<td>0.26 0.19</td>
<td>0.05 0.18</td>
<td>0.14</td>
<td>0</td>
</tr>
<tr>
<td>ZNPC-ctrl</td>
<td>0.33 -0.15 -0.35</td>
<td>0.66 -0.24</td>
<td>-0.44 0.2</td>
<td>-0.67</td>
<td>0</td>
</tr>
<tr>
<td>pH₀</td>
<td>5.09 5.17 5.09</td>
<td>5.2 5.37 5.3</td>
<td>5.07 5.18</td>
<td>5.22</td>
<td>4.96</td>
</tr>
<tr>
<td>ZNPC</td>
<td>5.79 4.91 5.34</td>
<td>5.54 4.95 5.33</td>
<td>5.5 5.06</td>
<td>5.15</td>
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<td>HVM kiawe</td>
<td>Soil alone</td>
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**Difference**

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<td>0.36 2</td>
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Characterization

- 130-190°C: cellulose and lignin begin to decompose
- >200°C carbonization begins, nitrogen volatilizes, 760°C to vaporize K and P
- **Cellulose** and pectin: up to 200°C, complex glucans form
  - >270°C, new aliphatic structures detected by NMR: aliphatic C, phenol and/or furan C, aromatic C, and carbonyl C
  - From carbohydrate char at 250°C to being dominated by phenols, furans, aromatic C at 350°C
  - >300°C, furan-like compound products. Condensation sites: nonvolatile anhydroglucose cores in side chains...glue for nonvolatile residues...more heating=furan polymer to aromatic polymer
  - PAHs detected when heated 300-600°C Diels Alder cycloaddition
- **Pectin** oxidized at 550°C totally
- Change in volatile composition: furans, pyronones, anhydrosugars and fufural at low T to phenol, catechol, and subst-phenols at high T
- At 200°C: NMR detected aliphatic, O-aryl, aryl, carbonyl, further heating=depolymerization and greater aromatic C with lesser amounts of ketones and aliphatic C at 550°C

- **Lignin**
  - Common monomeric units of polymer=phenylpropanol linked by ether bond or C-C
  - Heating lignin yields volatiles, mostly methoxyphenols=highest yield between 500 and 600°C
  - 40-60% volatilized at 450°C and 740°C
  - Heating from 250 to 400°C diminishes phenolic C and alcoholic C yields and removed aromatic substitutions
  - Fused ring formation at 400-500°C
  - Dehydration reactions predominate at lower T and decarboxylation at high T

Proteins: decompose systematic and random depolymerization rxns
Tar = defined as the VOLATILES?

Overall reactions: Lower T dehydration, dehydrogenation and degradation of O-alkyl C
350°C, more stable alkyl C and carboxyl C is removed and only part of recalcitrant, cyclic, or branched paraffinic structures remain in a condensed matrix, and increase in aryl C. Aryl:alkyl ratio as index of charring?

Paraffinics and sterols are more stable than fatty acids (GCMS)
Synthesis of new aromatic CL demethoxylation as decreasing methoxyphenol:phenol ratio
350°C: atomic C:O ratio=3 (Baldock and Smernik, 2002), shows that furans, anhydrosugars and structures from cellulose are important part of char
Atomic C to H=almost every second aromatic C is connected to H
Raw kiawe=contained molecules typical of plant material
- Straight chain aromatic= octacosane. Nonacosane=fuel; sterols-plant cholesterols
- Much less in corncob feedstock but typical plant materials
- 23% VM corncob
  - Myristic aldehyde: fatty acid derivative? Benzene ring, ether bonds, C=O
  - Dimethylethyl phenol: phenol with C-C, and OH
  - Dodecyl acrylate: alkyl chain with oxygen substition (ester bond C=C=O and C-O-C
  - Oleamide: amide of fatty acid oleic acid
  - Propanoic acid: HO-C=O and C-C-C

- 63% VM corncob
  - Ethyl phenol: phenol with ethyl group
  - Ethyl guaiacol: phenol with ethyl group and ether group
  - Vinyl guaiacol: pyrolysis product of lignin: phenol with ether group and C=C
  - Syringol: phenol with two ether groups C-O-C
  - Vanillin: aldehyde ether phenol, O=C-H
  - Tridecanol: CH chain with OH at end
  - Dodecyl acrylate: CH chain and C=C-C=O and C-OC (ester)
  - Methyloxyphenol: phenol with ether
  - Palmitic acid: fatty acid CH chain with carboxylic groups at end
  - FluoratheneL: PAH naphthalene or benzene stuck together with 5 member ring
  - Pyrene: 2 benzene and 2 two 6 member ring each with a double bond
Significant for incubations - 1 mo

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WEC:
- Time 0: HVM and others <.0001; Lvm and ctrl <.0001; HVM and HVMN 0.7917
- Time 1: HVM and others <.0001; Lvm and ctrl 0.0004; HVM and HVMN 0.2896
- Time 3: HVM and others 0.0826; Lvm and ctrl 0.0006; HVM and HVMN 0.4520
- Time 7: HVM and others 0.7126; Lvm and ctrl 0.0002; HVM and HVMN 0.1090
- Time 10: HVM and others 0.4403; Lvm and ctrl <.0001; HVM and HVMN 0.2838
- Time 14: HVM and others 0.0497; Lvm and ctrl 0.0004; HVM and HVMN 0.5453
- Time 21: HVM and others 0.9057; Lvm and ctrl 0.0065 HVM and HVMN 0.8519
- Time 28: HVM and others 0.5970; Lvm and ctrl <.0001 HVM and HVMN 0.2322
Significant for incubations - 2 mo

- FDA (autoregressive heterogeneous Proc Mixed)
  - Overall: Time; Txt; Time*Txt = p<0.001
    - Time 0 txt:p<0.001
      - ctrl v H-Ch 0.9529
      - H-Ch v L-Ch 0.5368
      - H-Ch v K-Ch 0.7307
      - H-Ch v H-ext 0.4690
    - Time 1 wk: p<0.001
      - ctrl v H-Ch 0.0086
      - H-Ch v L-Ch 0.0020
      - H-Ch v K-Ch 0.5819
      - H-Ch v H-ext 0.0059
    - Time 2 wk: p<0.001
      - ctrl v H-Ch <0.0001
      - H-Ch v L-Ch 0.0037
      - H-Ch v K-Ch 0.3359
      - H-Ch v H-ext 0.0382
    - Time 4 wk:
      - ctrl v H-Ch <.0001
      - H-Ch v L-Ch 0.0001
      - H-Ch v K-Ch 0.0335
      - H-Ch v H-ext 0.0009
    - Time 6 wk
      - ctrl v H-Ch 0.0138
      - H-Ch v L-Ch 0.0545
      - H-Ch v K-Ch 0.1279
      - H-Ch v H-ext 0.9378
    - Time 8 wk
      - ctrl v H-Ch 0.0099
      - H-Ch v L-Ch 0.0010
      - H-Ch v K-Ch 0.2072
      - H-Ch v H-ext 0.7869

- NH4 (autoregressive heterogeneous Proc Mixed)
  - Overall: Time; Txt; Time*Txt = p<0.001
    - Time 0 txt:p<0.001
      - ctrl v H-Ch 0.5913
      - H-Ch v L-Ch 0.7598
      - H-Ch v K-Ch 0.4603
      - H-Ch v H-ext 0.4390
    - Time 1 wk: p<0.001
      - ctrl v H-Ch 0.0245
      - H-Ch v L-Ch 0.2547
      - H-Ch v K-Ch 0.1064
      - H-Ch v H-ext 0.5963
    - Time 2 wk: p<0.001
      - ctrl v H-Ch 0.0091
      - H-Ch v L-Ch 0.0020
      - H-Ch v K-Ch 0.0015
      - H-Ch v H-ext 0.9921
    - Time 4 wk:
      - ctrl v H-Ch 0.0003
      - H-Ch v L-Ch 0.4346
      - H-Ch v K-Ch 0.0604
      - H-Ch v H-ext 0.1297
    - Time 6 wk
      - ctrl v H-Ch <.0001
      - H-Ch v L-Ch 0.1199
      - H-Ch v K-Ch 0.0130
      - H-Ch v H-ext 0.1018
    - Time 8 wk
      - ctrl v H-Ch <.0001
      - H-Ch v L-Ch <.0001
      - H-Ch v K-Ch <.0001
      - H-Ch v H-ext 0.0601

- NO3 (autoregressive heterogeneous Proc Mixed)
  - Overall: Time; Txt; Time*Txt = p<0.001
    - Time 0 txt:p<0.001
      - ctrl v H-Ch 0.0444
      - H-Ch v L-Ch 0.9516
      - H-Ch v K-Ch 0.7650
      - H-Ch v H-ext 0.0546
    - Time 1 wk: p<0.001
      - ctrl v H-Ch 0.0535
      - H-Ch v L-Ch 0.7974
      - H-Ch v K-Ch 0.1185
      - H-Ch v H-ext 0.7178
    - Time 2 wk: p<0.001
      - ctrl v H-Ch 0.0328
      - H-Ch v L-Ch 0.0020
      - H-Ch v K-Ch 0.0015
      - H-Ch v H-ext 0.9921
    - Time 4 wk:
      - ctrl v H-Ch 0.7976
      - H-Ch v L-Ch 0.0003
      - H-Ch v K-Ch 0.0096
      - H-Ch v H-ext 0.2979
    - Time 6 wk
      - ctrl v H-Ch 0.0017
      - H-Ch v L-Ch <.0001
      - H-Ch v K-Ch <.0001
      - H-Ch v H-ext 0.5777
    - Time 8 wk
      - ctrl v H-Ch 0.1143
      - H-Ch v L-Ch 0.0021
      - H-Ch v K-Ch 0.0001
      - H-Ch v H-ext 0.7300
Significance for 2-wk and Prussian Blue

- **FCU & FDA**
  - Sqrt transformed
  - Acetone extractable = A
  - 23% VM char = B
  - Extracted char = C (FDA) and B (counts)
  - Control = D (FDA) and C (counts)

- **Prussian blue**
  - Log transformed for to pass equal variance
  - HVM chars = A
  - Extracted = B
  - 7% VM cc = C
Mineralization slope

- Soil alone = A
- All charcoals = B
**Discussion of techniques**

- **GCMS**: control set chamber to 250°C. GC separates molecules by their partitioning properties in the columns. MS then charges ions. It identifies them by their mass to charge ratio. The time it takes to travel through the system is a function of its molecular weight.

- **FTIR**: collects infrared spectra. Shoots out infrared energy which certain frequencies are absorbed by molecules, which is characteristic of their structure. So, absorption = vibrational frequency. Different types of vibrations, known as vibration modes. Absorption bands: along wavenumbers—triple bonds, 2300 -2100; double, 1800-1500; and single (fingerprint) 1500 -1000.

- **NMR**: emit a magnetic pulse, nuclei absorb energy and radiates energy back at a specific resonance frequency. Two steps: (1) apply constant magnetic field and align or polarize magnetic nuclear spins (2) perturbation with pulse to observe nuclei. You can gain structural information about molecular groups by observing their shifts on the resonant frequency of the nuclei present.
2.2.2 FTIR

An FTIR-attenuated total reflectance (ATR) technique was employed to qualitatively analyze the functional groups in the 23% and 7% volatile matter corncob charcoals, 23% volatile matter kiawe charcoal, and the activated charcoal samples. Spectra were recorded within the 4,000 cm\(^{-1}\) to 400 cm\(^{-1}\) range with a resolution of 16 cm\(^{-1}\) by obtaining 256 scans on a Thermo Nicolet 380 spectrometer with the Smart Performer accessory. The interpretation of the FTIR spectra were intended for qualitative analysis only.

2.2.3 NMR

We used a 200 MHz Bruker DSX spectrometer (\(^{13}\)C frequency 50 MHz) equipped with a 4mm magic angle spinning (MAS) probe to obtain \(^{13}\)C NMR spectra of the 23% and 7% volatile matter corncob and 23% volatile matter kiawe charcoals. All analyses were conducted at a rotor spinning rate of 7 kHz. We improved quantitation with a relatively high spinning rate, which moves the spinning sideband signals outside of the \(^{13}\)C chemical shift range (i.e. 0 – 220 ppm) and prevents overlap with other signals. Cross polarization (CPMAS) were acquired by applying a 90 degree \(^{13}\)C excitation pulse, 1ms \(^{13}\)C contact pulse, two-pulse phase-modulated (TPPM) \(^{1}\)H decoupling, and a 3 s recycle delay between scans.

The highly aromatic structure of charcoal makes quantitative characterization of charcoals by CPMAS NMR difficult since it inhibits efficient \(^{1}\)H-\(^{13}\)C polarization transfer. Thus, CPMAS NMR spectra are best regarded as semi-quantitative. We overcame this limitation by using a direct polarization pulse sequence (DPMAS). We utilized a 20 degree excitation pulse, which reduced the recycle delay from 100 s to 5 s and increased the signal-to-noise per unit time by a factor of 16 relative to spectra acquired with a 90 degree \(^{1}\)H excitation pulse. We acquired DPMAS spectra with \(^{1}\)H-\(^{13}\)C dipolar-dephasing by inserting a 50 \(\mu\)s dephasing delay prior to the TPPM decoupling, which are devoid of signals from carbon atoms with a directly bonded hydrogen atom (C-H). Due to the behavior of aromatic model compounds, we applied a 10% intensity correction to signals in the dipolar-dephasing NMR spectra to compensate for relaxation during the 50 \(\mu\)s delay.

We subtracted background signals arising from carbon-containing probe and rotor components from each of the charcoal spectra so that we could quantitatively interpret the peak areas obtained by DPMAS as measurements for carbon functional groups. The quantitative reliability of all NMR experiments has been assessed by calculating (see Equation 1) the percentage of sample carbon observed in the spectrum (\(C_{\text{obs}}\)), using a procedure known as spin counting (Smernik & Oades; 2000).

\[
\text{Charcoal Structure Elucidation}
\]

We used a novel \(^{13}\)C-\(^{1}\)H dipolar dephasing technique based upon the DPMAS sequence (described above) for a quantitative measure of the protonated versus the bridgehead aromatic carbons within the charcoal backbone structure. We estimated the average the number of aromatic carbon atoms fused together in a cluster, average number of oxygen atoms per cluster, and the average number and length of the alkyl side chains attached to each cluster of aromatic carbons, using the algorithms derived by Solum et al., (1989).

2.2.4 GC-MS

The chemical analysis was performed by GC-MS for the 63%, 23%, 7% VM and acetone-extracted corncob charcoal; 23% VM kiawe charcoal; activated charcoal; and raw corncob husk and kiawe wood. We extracted 1-g of each sample by sonication with acetone for 30 min. The extracts were filtered then analyzed with a Varian CP-3800 gas chromatograph interfaced with a Varian 1200 mass spectrometer. A Factor Four VF5-MS (Varian) capillary column was used. The GC-MS ion source and transfer lines were kept at 200 and 250°C respectively, and the analysis was conducted in electron impact at 70 eV, full scan mode (50-550 u range). The NIST 2002 mass spectral library was used for compounds mass spectral identification.

2.2.5 Prussian Blue for Phenols

Prussian blue analysis to measure total phenol content followed the protocol outlined by Stern et al. (1996). Samples of 23% and 7% volatile matter corncob and 23% volatile matter kiawe charcoals were extracted with 90% acetone, in triplicate. One hundred microliters of the extract from each sample was transferred into 30-ml test tubes. Three ml of ferric ammonium sulfate (0.1 \(M\) Fe\((\text{NH}_4\)\)\(2\)\(SO_4\))\(_2\) in 0.1 \(M\) HCl was then added to successive samples at 1.0 minute intervals. Exactly 20 minutes after the ferric ammonium sulfate additions, 3.0 ml of potassium ferricyanide (0.008 \(M\) \(K_3\text{Fe(CN)}_6\)) was added to each sample, successively. Exactly 20 minutes later, the absorbance was read at 720 nm.