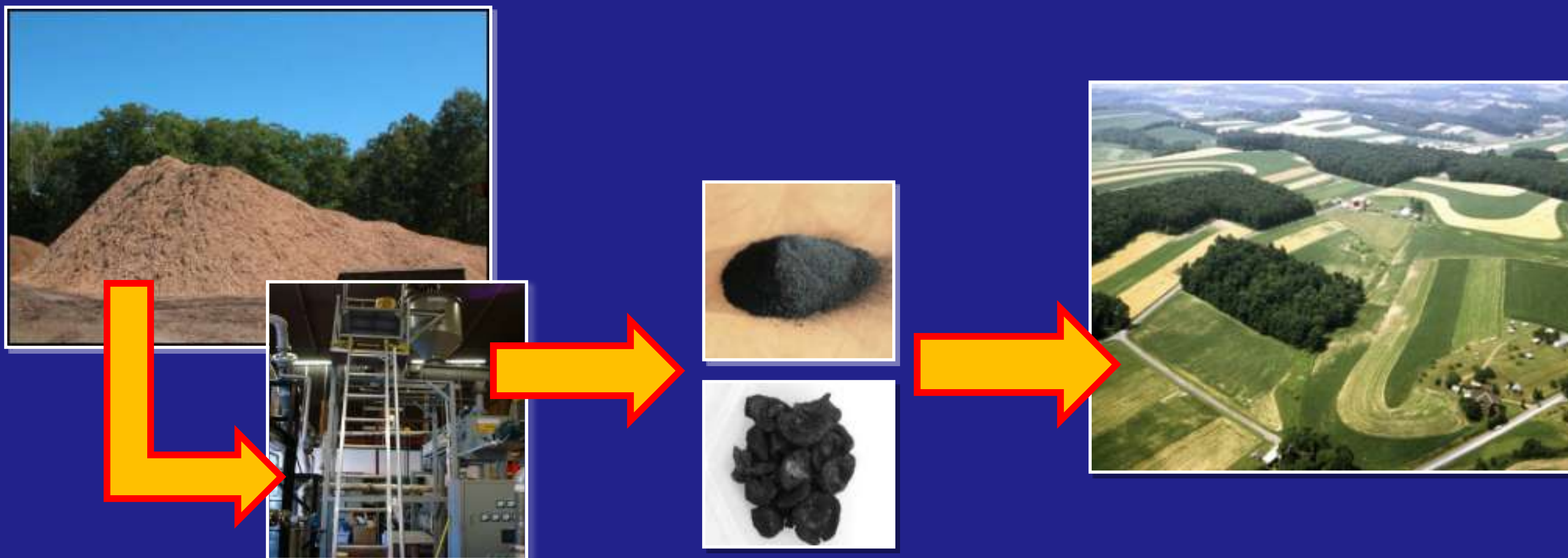
Biochar:
Impacts on Soil Microbes and the Nitrogen Cycle



Kurt Spokas

USDA-ARS, Soil and Water Management Unit, St. Paul, MN
Adjunct Professor University of Minnesota – Department of Soil, Water and Climate

Agricultural Research Service (*ARS*)

• In-house scientific research agency for the United States Department of Agriculture (USDA).

Goal: Finding solutions to agricultural problems that affect Americans every day, from field to table

- 2,500 scientists
- 6,000 other employees
- 1,000 research projects within 20 National Programs
- 100 research locations including a few in other countries
- $1.1 billion (USD) fiscal year 2010 budget

USDA

Agricultural Research Service

St. Paul, MN

45º N 93º W

Annual Average Temperature

7.44 C

Average Annual Precipitation

746 mm

Record low temperature -40 C

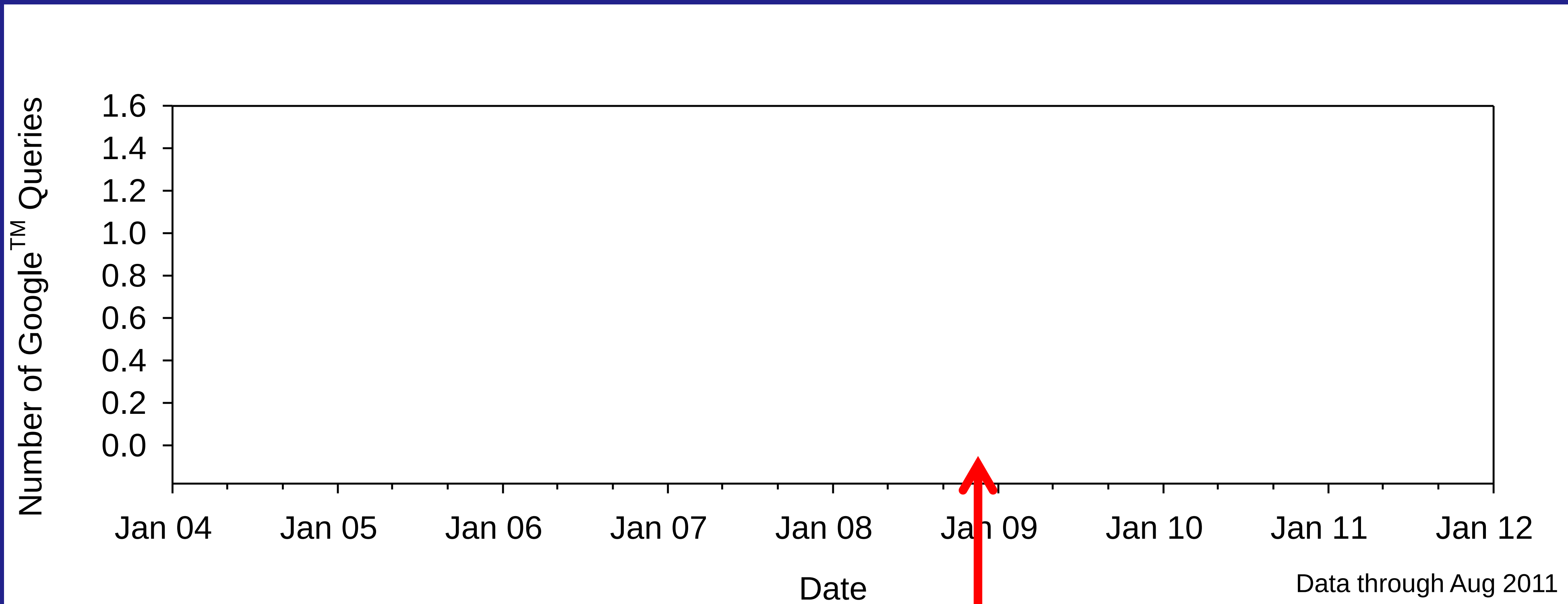
Record warm temperature 42 C

Biochar: What is it ?

"Those who do not learn from history are doomed to repeat it"

George Santayana

Biochar – Google™ Timeline



1998 - First use of *biochar* to describe the solid residue from biomass pyrolysis (Bapat and Manahan, 1998)

10 years later

Dec. 2008 – Biochar linked in newsfeed story as a potential abatement to climate change; even though scientifically was mentioned over 20 years prior (~1985)

Black Carbon (definition)

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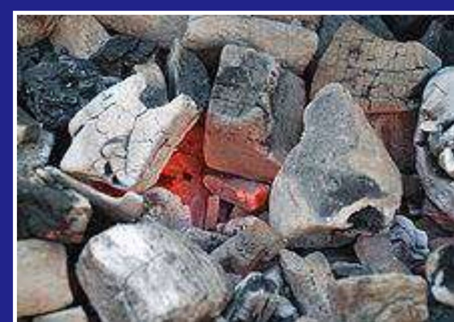
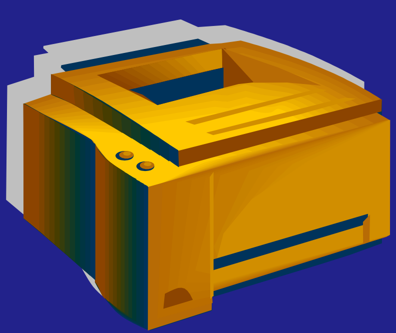
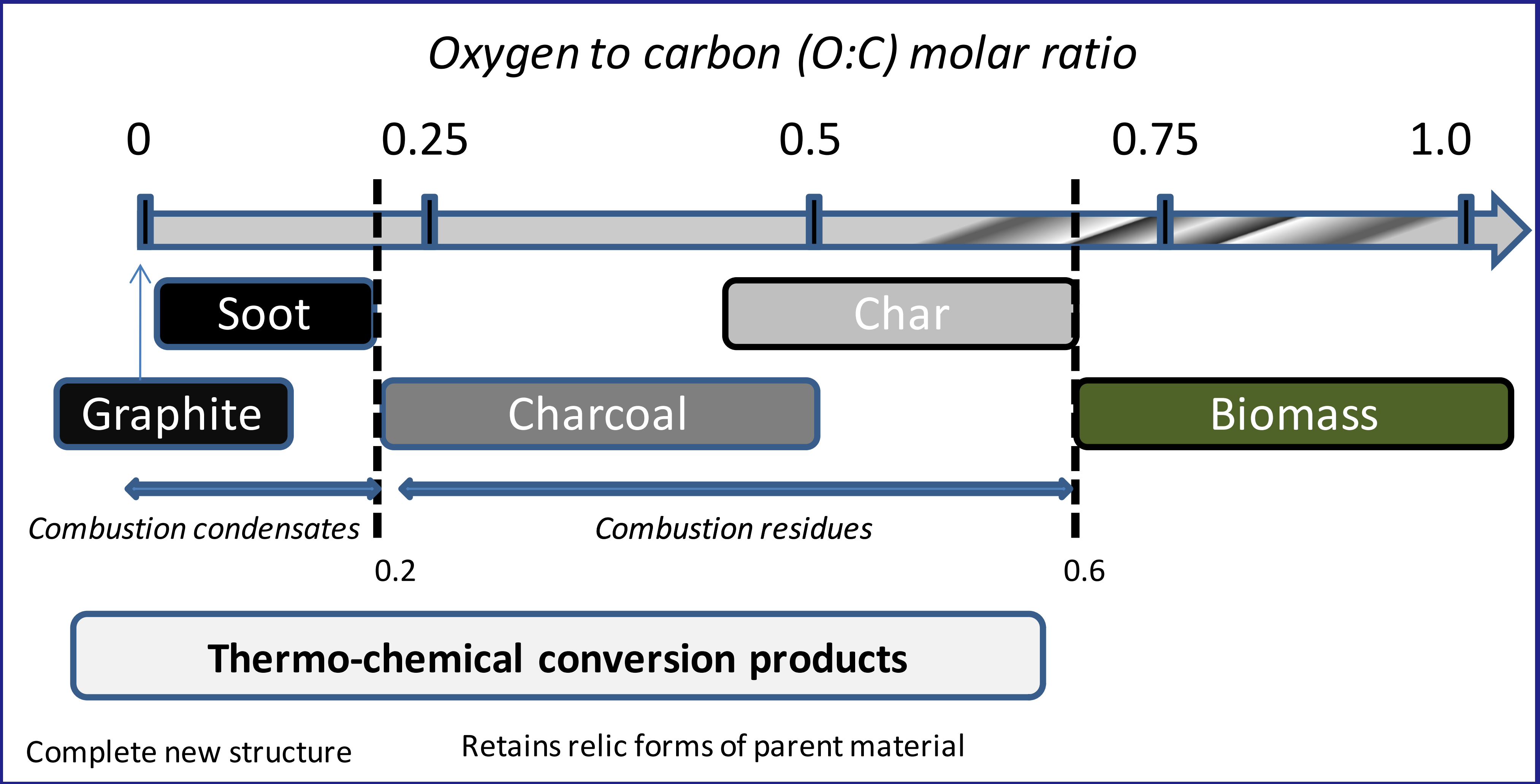
•*Black carbon* is the range of solid residual products resulting from the chemical-thermal conversion of any carbon containing material (e.g., fossil fuels and biomass) (Jones et al., 1997)


Black Carbon Continuum

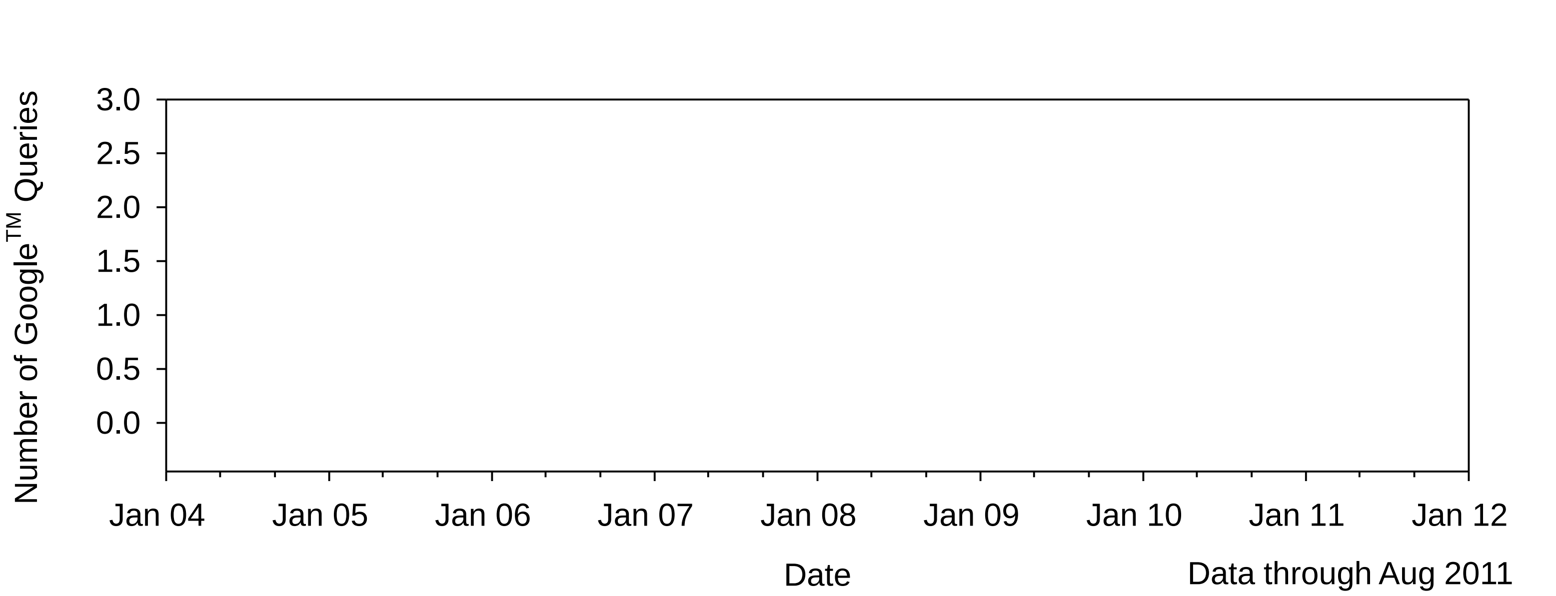


Adapted from Hedges et al., 2000; Elmquist et al., 2006; Spokas, 2010

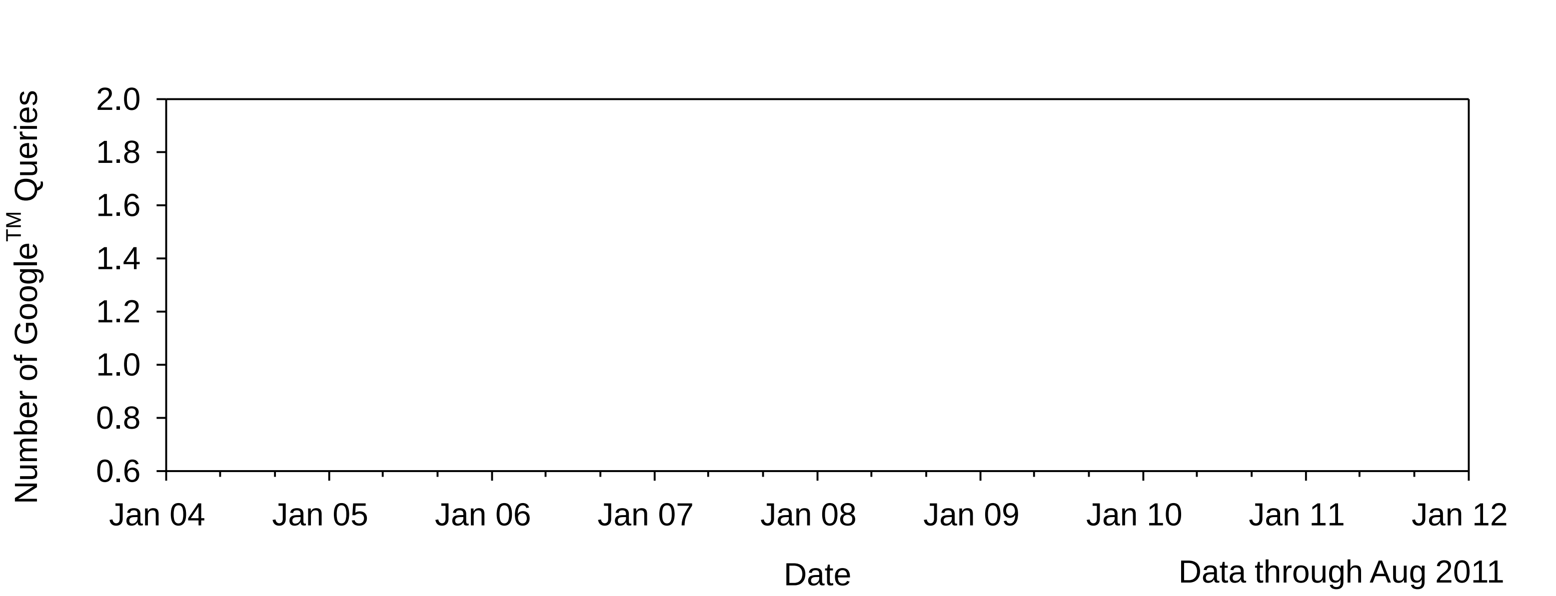
Problem → Lack of nomenclature uniformity

(Jones et al., 1997)

Back to Google Search Trends



Black Carbon



Charcoal

Formation of Black Carbon: Pyrolysis

- Pyrolysis is the chemical decomposition of an organic substance by heating
  - Does not involve reactions with oxygen
    - Typically in the absence of oxygen
  - Pyrolysis is also used in everyday activity –

    Cooking → roasting, baking, frying, grilling
- Also occurs in lava flows and forest/prairie fires

Wide Spectrum of Pyrolysis

Both temperature and time factors:

- High temperature pyrolysis
  →gasification (>800 ºC) {+ O_2 }

- "Fast" or "Slow" pyrolysis (300-600 ºC)
  - Fast pyrolysis
    - 60% bio-oil, 20% biochar, and 20% syngas
    - Time = seconds
  - Slow pyrolysis
    - Can be optimized for char production (>40% biochar yields)
    - Time = hours

Pyrolysis unit in Florence, SC (USDA-ARS)

Others…

Biochar: New purpose not a new material

Pyrolysis, carbonization, and coalification are well establish conversion processes with long research histories

Except:

Prior emphasis:

Conversion of biomass to liquids (bio-oils) or gaseous fuels and/or fuel intermediates

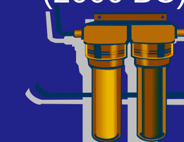
Solid byproduct (biochar) has long been considered a “*undesirable side product*”

(Titirici et al., 2007)

Cave Drawings
(>10,000 to 30,000 BC)

Used as fuel
(3000-4000 BC)

Water filtration
(2000 BC)



Charcoal production
(15^{th} century)

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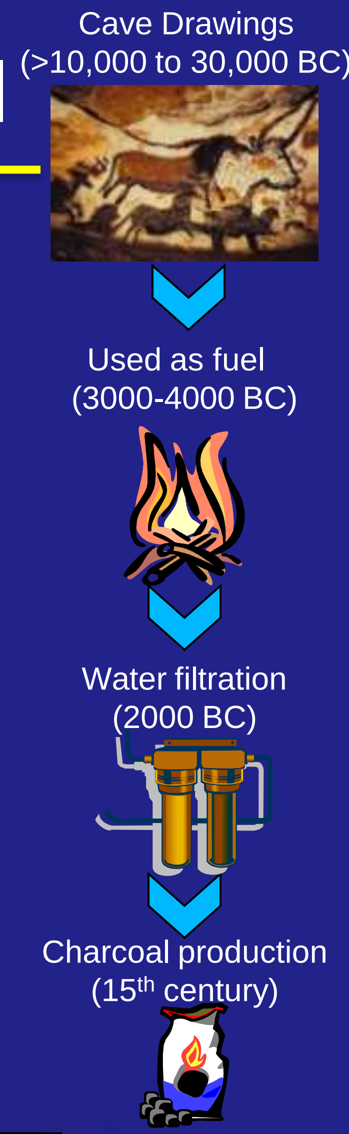

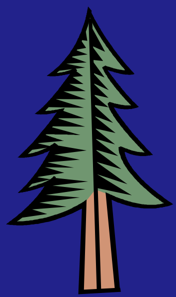

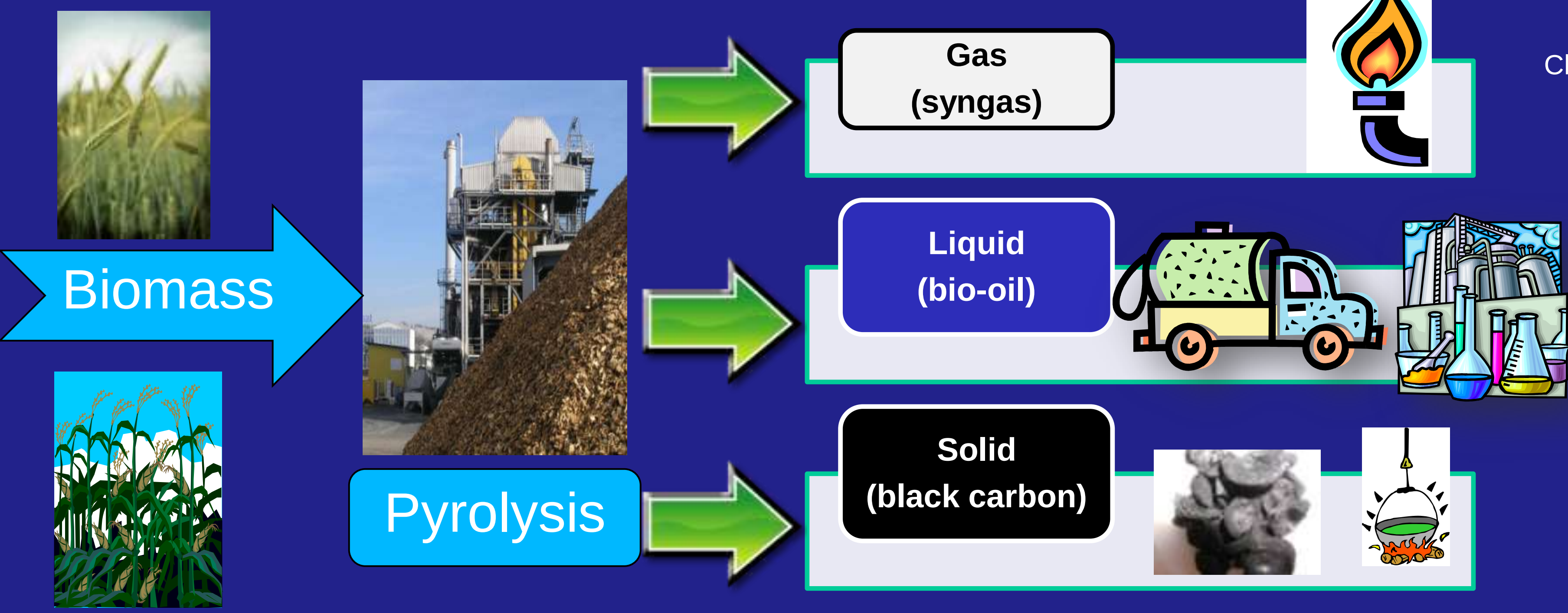

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(Titirici et al., 2007)

- What is new?

The use (or purpose) for the creation of charred biomass

- Atmospheric C sequestration

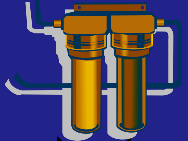
Dates to 1980's and early 2000's

(Goldberg 1985; Kuhlbusch and Crutzen, 1995; Lehmann, 2006)

Cave Drawings (>10,000 to 30,000 BC)

Used as fuel (3000-4000 BC)

Water filtration (2000 BC)

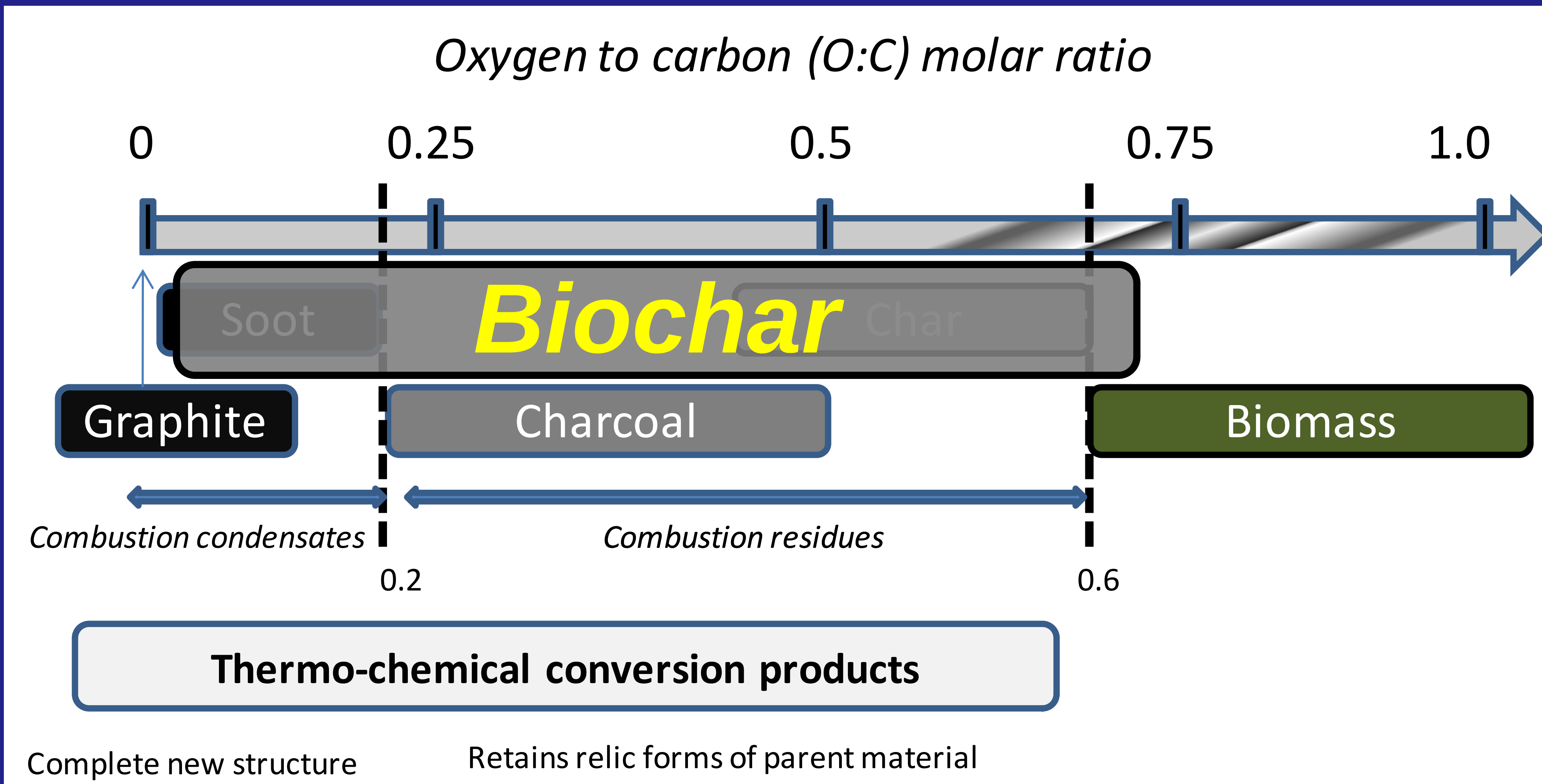


Charcoal production (15^{th} century)

Climate Change Mitigation (1980's)

Biochar: Black Carbon Continuum

Biochar – Spans across multiple divisions in the Black C Continuum
However, *biochar is NOT a new division or material…*



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

Biochar




Gaining significant attention:

- 1. Carbon Storage
  - Biochar can store atmospheric carbon, potentially providing a mechanism for reduction in atmospheric CO_2 levels
- 2. Soil Improvements
  - Improve water quality
  - Improve soil fertility
  - Reduce GHG emissions
- 3. Bioenergy

Comparisons of “Natural” vs. Synthetic

Natural Black Carbon (*Biochar?*)

-Heterogeneous feedstock

- <u>Impurities</u>
  - Soil and oxygen
    Minerals (metals) alter yields
    (e.g. Robertson, 1969; Bonijolya et al., 1982; Baker, 1989)
- <u>Multiple feedstock sources</u>
  - Species and types

-Variable temperature

- 80 to 1000 ^{o}C

-Air cooled/Precipitation/Solar (UV)

- Exposed to environmental conditions

Synthetic (Pyrolysis) Biochar

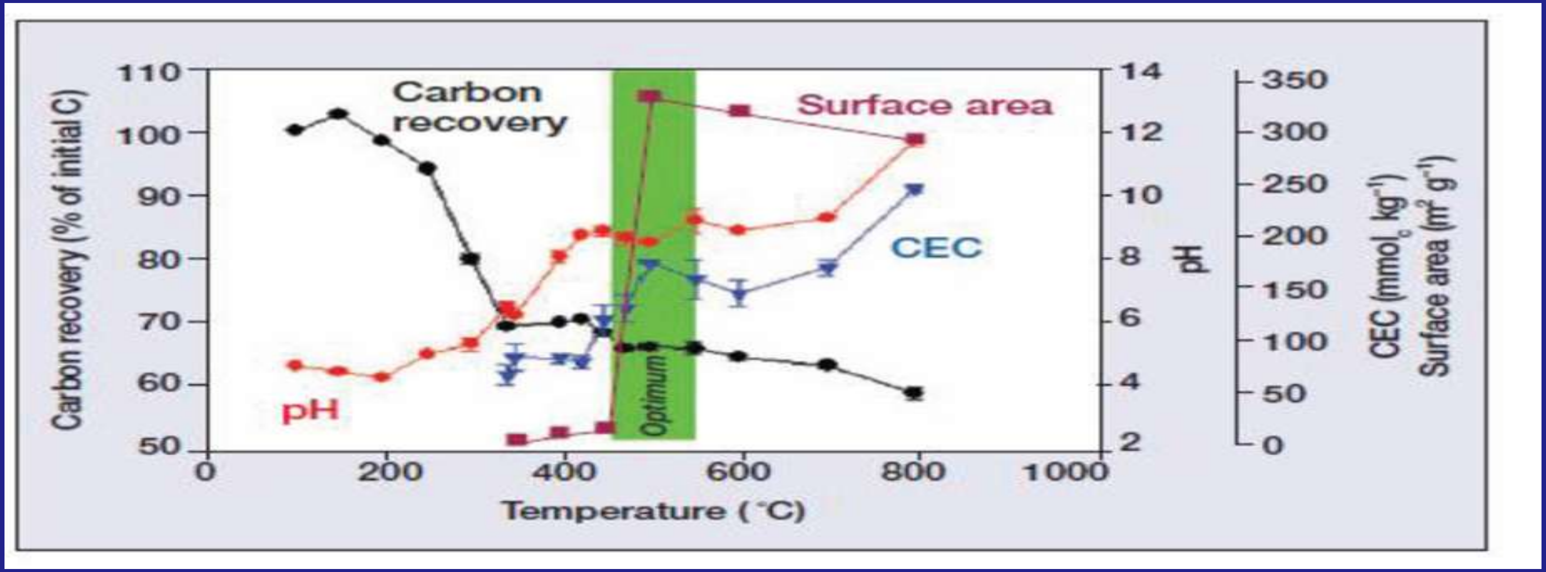
-Pure homogeneous feedstock

-“Constant” temperature

- Industrial Process

-Typically cooled under anaerobic conditions (no water)

Influence of production conditions



(Lehmann, 2007)

Biochar

- Solid residue remaining after the heating of biomass materials (renewable) without oxygen (incomplete combustion) for the purpose of carbon sequestration

Biomass Materials

Easily degradable
(0-5 yrs)

Pyrolysis

Recalcitrant carbon form
(black carbon)
(>50 to 1,000,000 yrs?)

Biochar: Soil Application

- The assumed target for biochar has been soil application
- Focus has been on “creating” *Terra Preta* soils

Observations of increased soil fertility and productivity.
Postulated from ‘slash and burn’ historic charcoal additions

- Biochar (BC) Hypothesized involved in humic acid formation

(Haumaier and Zech, 1995)

Biochar: Soil Application History

However, on the other side:

- Wood distillation plants [1800-1950's]
  - Wood pyrolysis – source of chemicals and energy prior to petroleum (fossil fuels)
  - Some historic plants on US-EPA Superfund site list

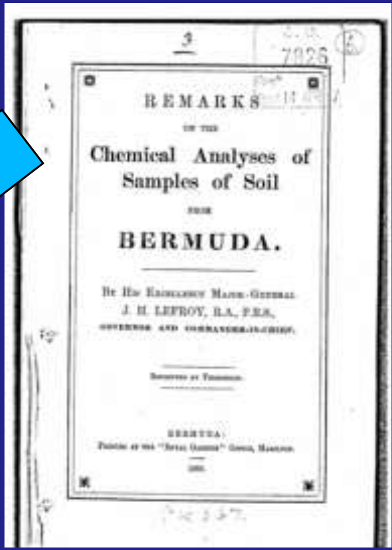
- Other charcoal sites
  - Not always productive
    - Reduced seed germination
    - Reduced plant growth

(BEGLINGER AND LOCKE, 1957)

Soil Application… Long History

Applications date back to the beginning of modern science [1800's]:

Ashes (see also *Potash*) "constitute an important class of manures, differing, however, in their effects according to the substance which has undergone the process of burning, and the manner in which the process has been accomplished. The ashes of all vegetable substances consist principally of those substances which plants require, as charcoal, lime, phosphoric acid, and alkaline salts. Of these charcoal or carbon is the most valuable, and hence to secure it in the greatest quantity the process of burning should be carried on as slowly as possible, and this is best effected by covering up the mass while burning and admitting no more air than just sufficient to keep up a smouldering fire. The ashes of all vegetables contain almost the same constituent parts, and are found useful in all soils and to the majority of crops. They should always be applied when newly burned, as they lose much of their value by keeping even although kept under cover. A medium quantity of ashes may be taken as 1 lb. weight to the square yard."* Coal ashes finely screened are also useful as manure, but less so than wood ashes. The ashes of sea weed, known in England as kelp, contain carbonate of soda and salts of potash, and are much used



(LeFroy, 1883)

Quote is from a 1833 report

Application rate ≈5000 lb/ac (5500 kg/ha)

Soil Application… Long History

Applications date back to the beginning of modern science [1800's]:

And even earlier…

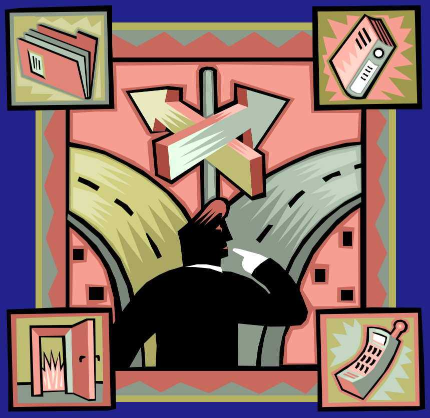
Fire pits built on soil…

Ancient Egyptians - pyroligneous acid (bio-oil)

-used for embalming

Soil Application

- Recent compilation of historical and recent biochar applications:



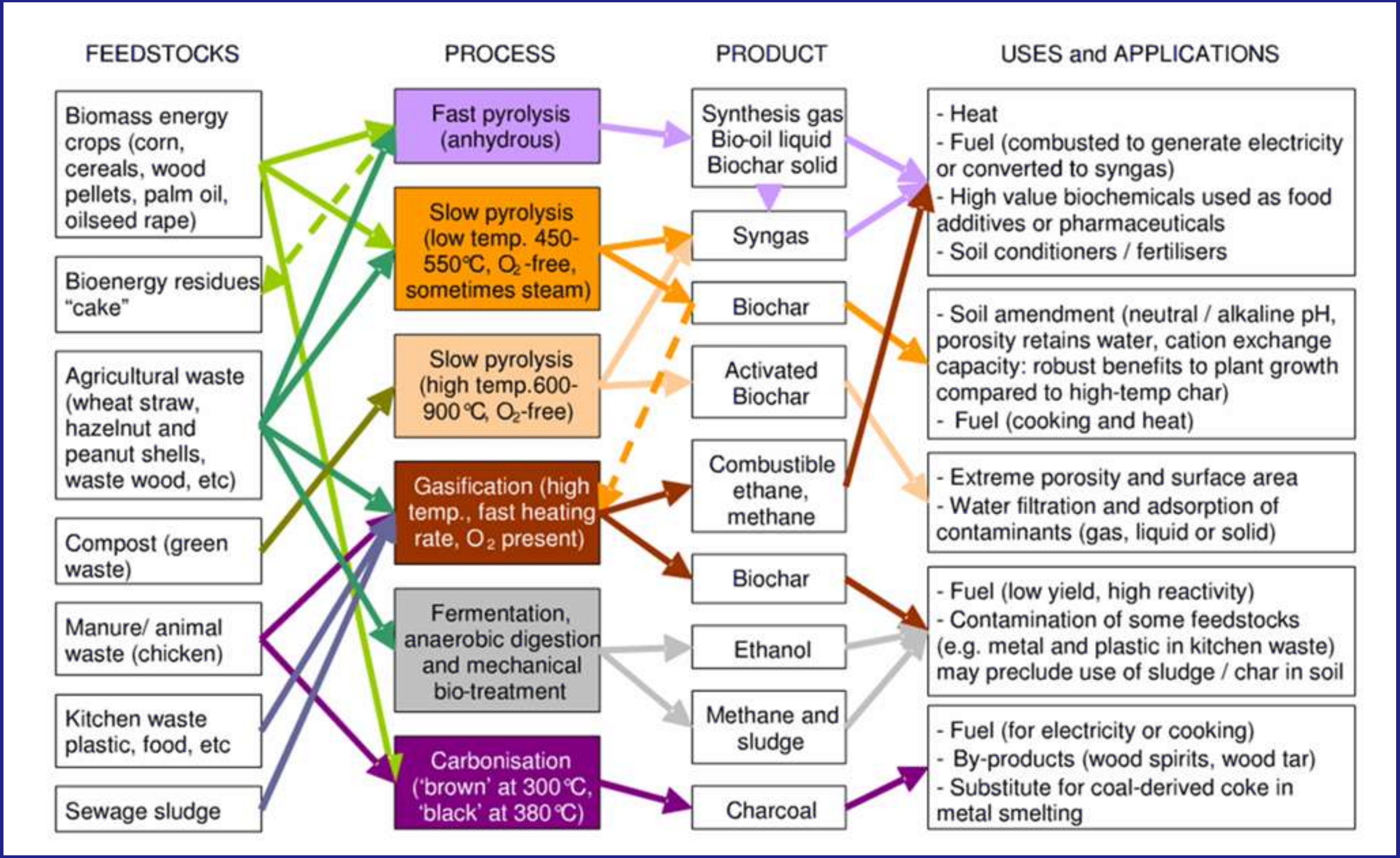
  - 50% positive,
  - 30% no effect, and
  - 20% negative impacts on growth and/or yield

(Spokas et al., 2011)

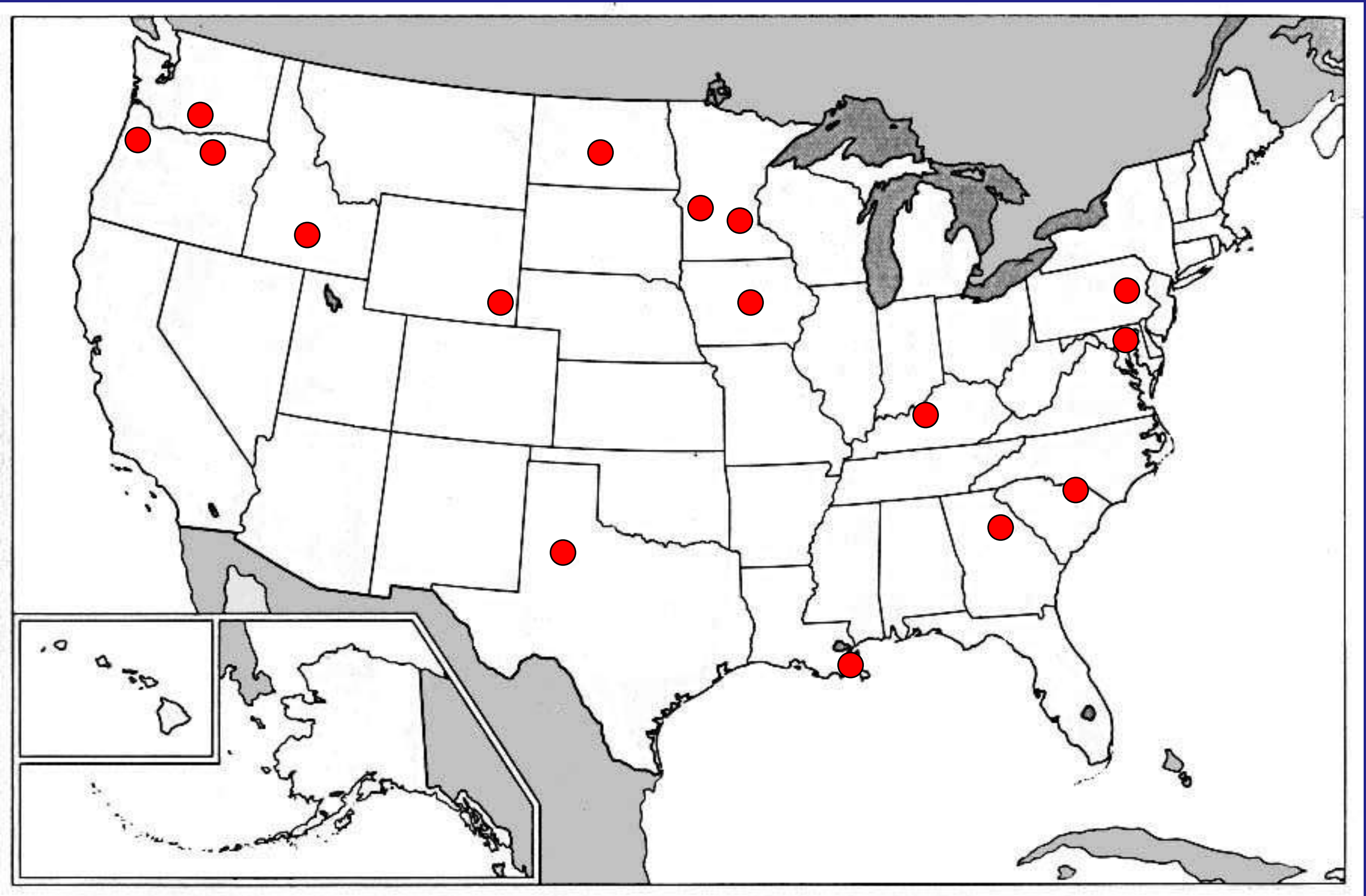
  - *However, <u>should not</u> be used as a basis for forecasting outcomes → Publication bias*

(Møller and Jennions, 2001)

From Sohi (2009)

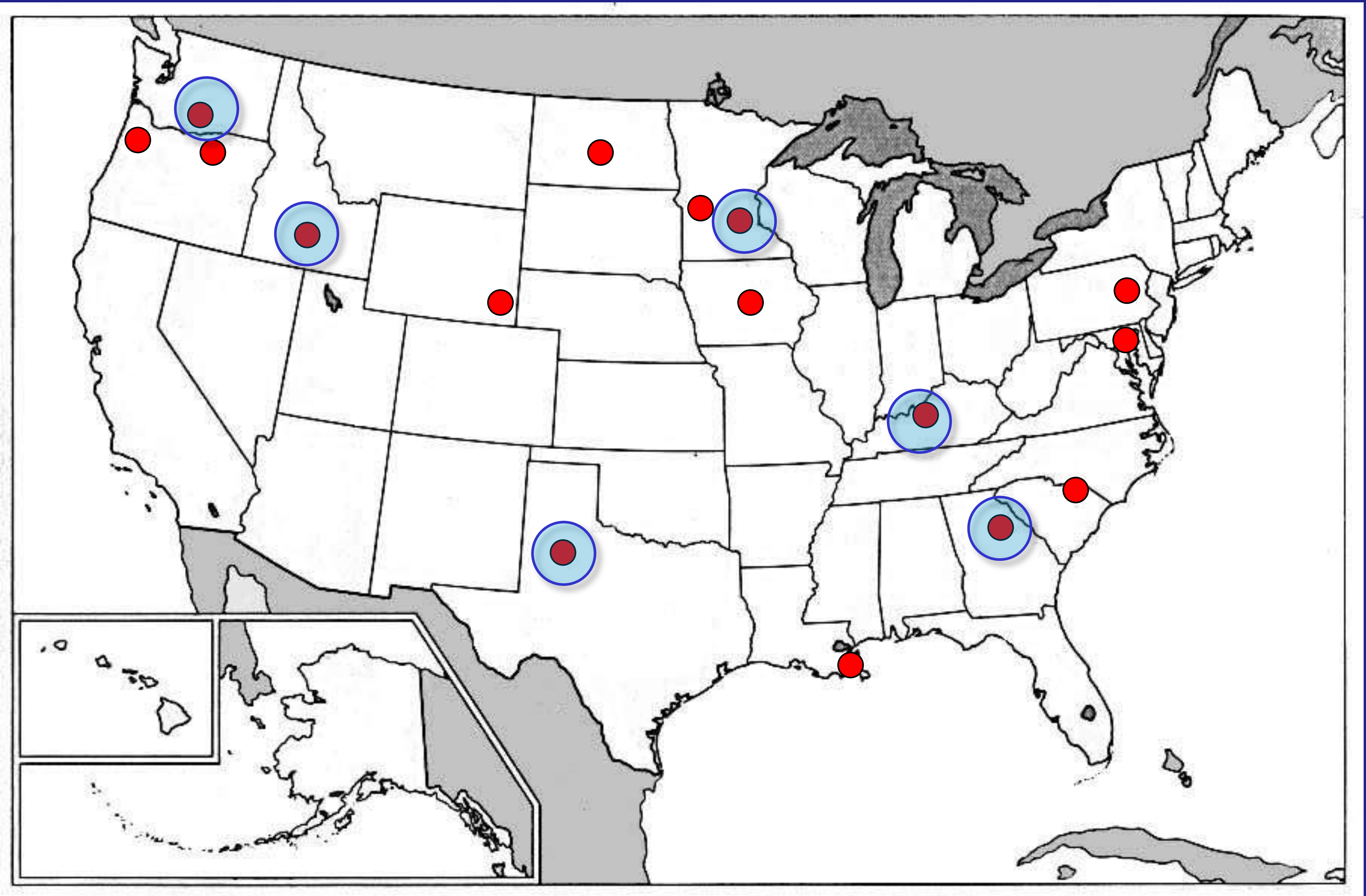


USDA-ARS Biochar and Pyrolysis Initiative



16 Locations – Coordinated Multi-location Research Activities

USDA-ARS Biochar and Pyrolysis Initiative



6 Locations – Coordinated field plot experiment using same hardwood biochar

ARS Biochar Research

Multi-location project

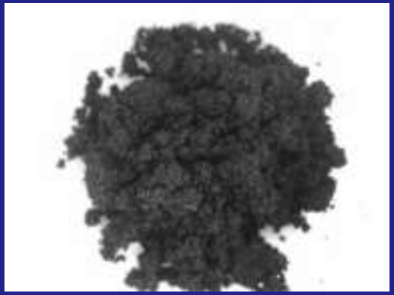
- 6 ARS locations:
  - Ames, IA; Kimberly, ID; St. Paul, MN;
  - Big Spring, TX; Florence, SC; Prosser, WA.
    - +additional sites in the near future

- Biochar used in replicated field plots
- Continuous corn (same crop for comparison)
- In addition to following crop yield and soil carbon:
  - ✓ Soil gas concentrations and trace gas fluxes
  - ✓ Seedling Emergence/Initial seedling growth rates

Biochar Impacts on Soil Microbes & N Cycling

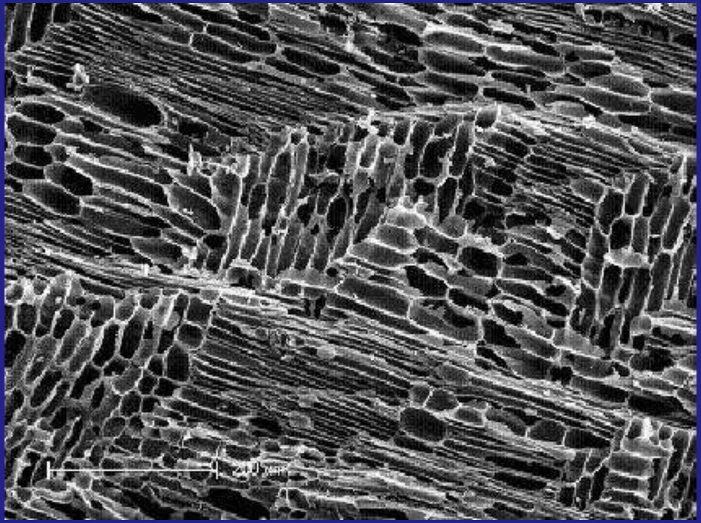
- 90+ different biochars being evaluated
- 19 different biomass parent materials
  - Hardwood, softwood, corn stover, corn cob, macadamia nut, peanut shell, sawdust, algae, coconut shell, sugar cane bagasse, switchgrass, turkey manure, chicken feathers, distillers grain
- Represents a cross-sectional sampling of available "biochars"
  - C content 1 to 84 %
  - N content 0.1 to 2.7 %
  - Production Temperatures 350 to 850 ^{o}C
  - Variety of pyrolysis processes
    - Fast, slow, hydrothermal, gasification, microwave assisted (MAP)

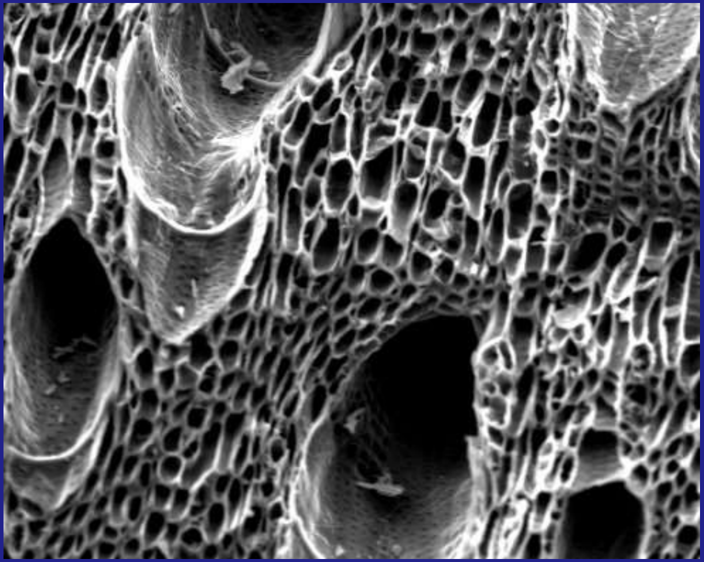


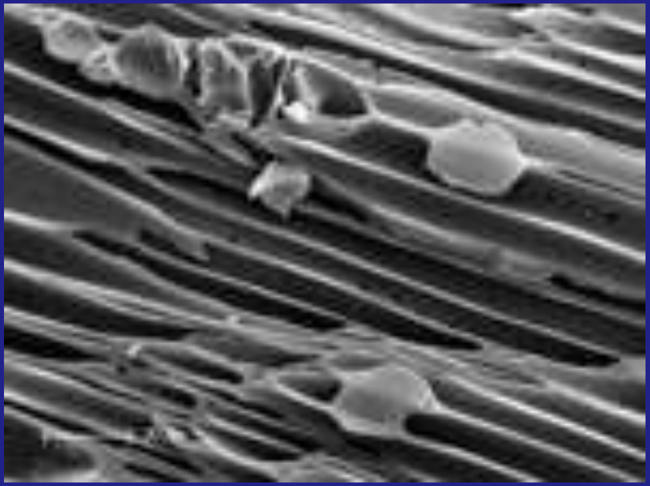



Biochar: Structure

Biochar : Majority of SEM images still show relic structures in the biochar







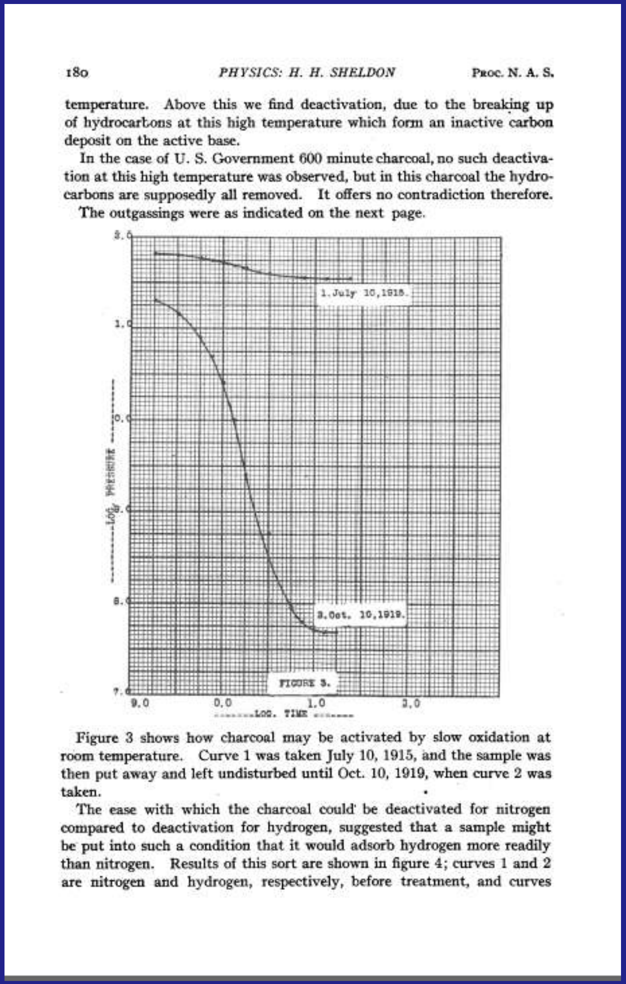
Post-processing of Biochar (Activation)

- Charcoal can be customized in terms of sorptive behavior by activation
  - "Designer Biochar" (J. Novak)
  - Processes:
    - <u>Thermal</u> and/or <u>chemical</u>
      - $ZnCl_2$, steam, acid, base, etc.

- However:

  Surface modification of charcoals <u>also occurs in air at ambient conditions</u>

  3 fold increase in N_2 sorption: 4 year storage (Sheldon, 1920)


180 *PHYSICS: H. H. SHELDON* PROC. N. A. S.

temperature. Above this we find deactivation, due to the breaking up of hydrocarbons at this high temperature which form an inactive carbon deposit on the active base.

In the case of U. S. Government 600 minute charcoal, no such deactivation at this high temperature was observed, but in this charcoal the hydrocarbons are supposedly all removed. It offers no contradiction therefore.

The outgassings were as indicated on the next page.

Figure 3 shows how charcoal may be activated by slow oxidation at room temperature. Curve 1 was taken July 10, 1915, and the sample was then put away and left undisturbed until Oct. 10, 1919, when curve 2 was taken.

The ease with which the charcoal could be deactivated for nitrogen compared to deactivation for hydrogen, suggested that a sample might be put into such a condition that it would adsorb hydrogen more readily than nitrogen. Results of this sort are shown in figure 4; curves 1 and 2 are nitrogen and hydrogen, respectively, before treatment, and curves

MN Department of Agriculture Project

- Examining the bioaccumulation of sorbed chemical species in specialty crops

- Impacts on yield and growth

- Field and laboratory components

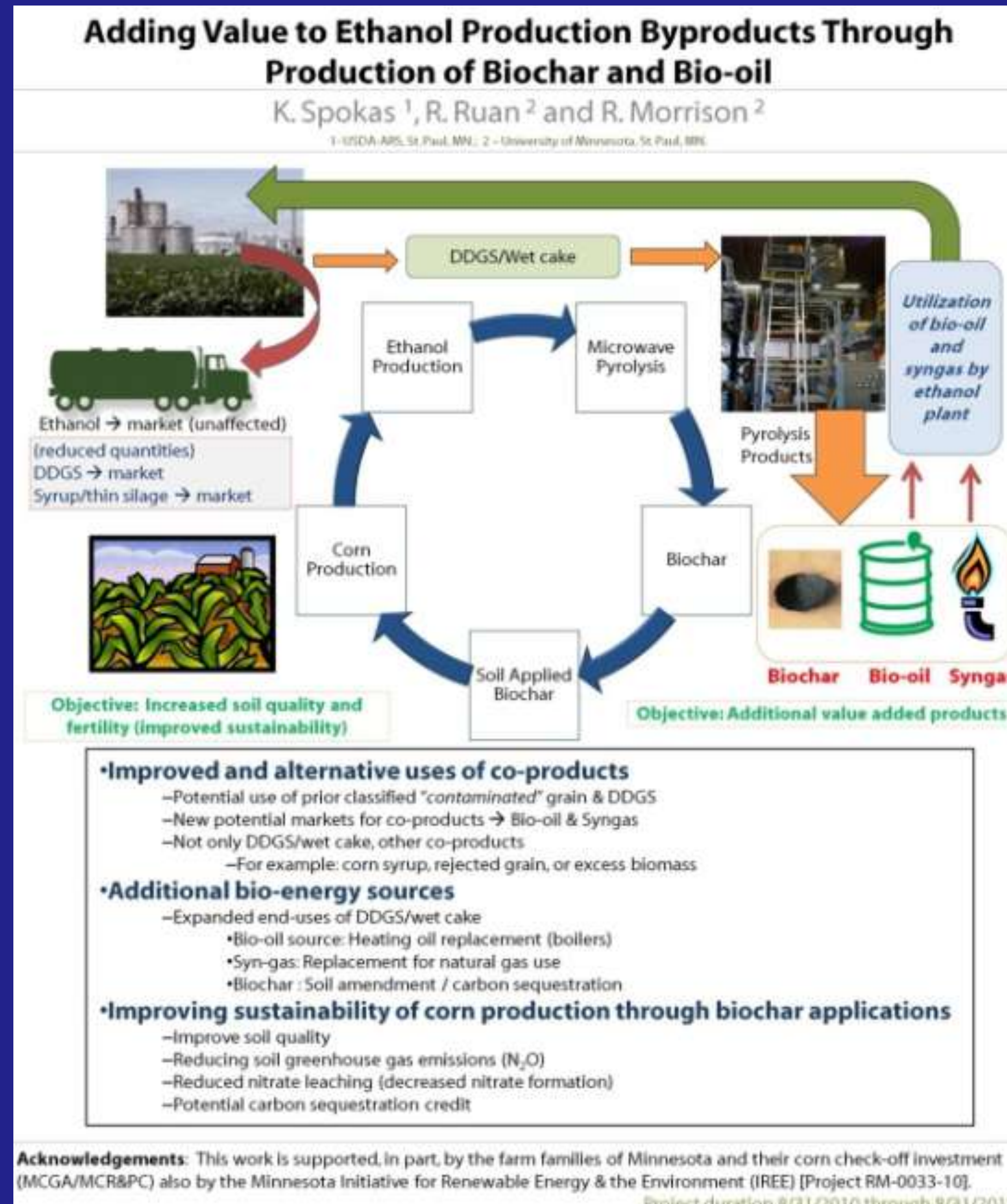
MINNESOTA DEPARTMENT OF AGRICULTURE

MN Corn Growers Association Project

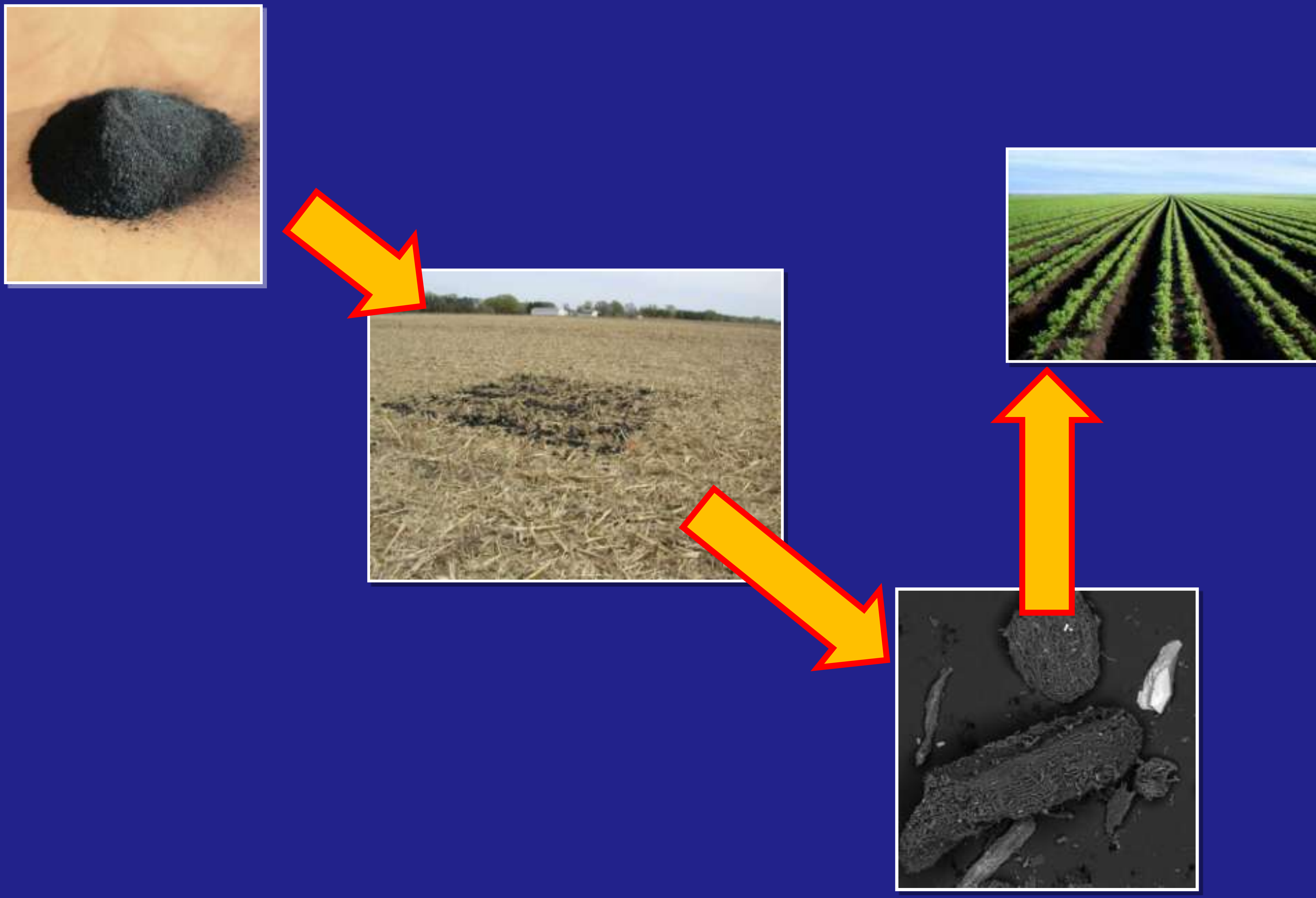
MinnesotaCorn

- Improved & alternative use of distillers grain through microwave assisted pyrolysis

- Examining the potential impacts of distillers grain biochar on soil system – Potential closing the nutrient loop of corn production

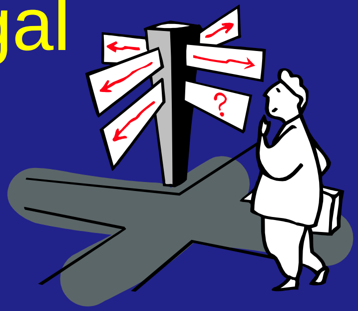


Biochar Interactions



Proposed Biochar Mechanisms

1. Alteration of soil physical-chemical properties
   - ✓ pH, CEC, decreased bulk density, increased water holding capacity
2. Biochar provides improved microbial habitat
3. Sorption/desorption of soil GHG and nutrients
4. Indirect effects on mycorrhizae fungi through effects on other soil microbes
   - ✓ Mycorrhization helper bacteria → produce *furan/flavoids* beneficial to germination of fungal spores



Warnock et al. (2007)

Biochar: Soil Stability

- Over a 100 year history of research

  Potter (1908) – Initial observation of fungi/microbial degradation of lignite (low grade coal/black carbon)

Biochar Degradation Study	Residence Time (yr)
Steinbeiss et al. (2009)	<30
Hamer et al. (2004)	40 to 100
Bird et al. (1999)	50-100
Lehmann et al. (2006)	100's
Baldock and Smernik (2002)	100-500
Hammes et al. (2008)	200-600
Cheng et al. (2008)	1000
Harden et al. (2000)	1000-2000
Middelburg et al. (1999)	10,000 to 20,000
Swift (2001)	1,000-10,000
Zimmerman (2010)	100's to >10,000
Forbes et al. (2006)	Millennia based on C-dating
Liang et al. (2008)	100's to millennia

Possible Stability Explanation → O:C Ratio

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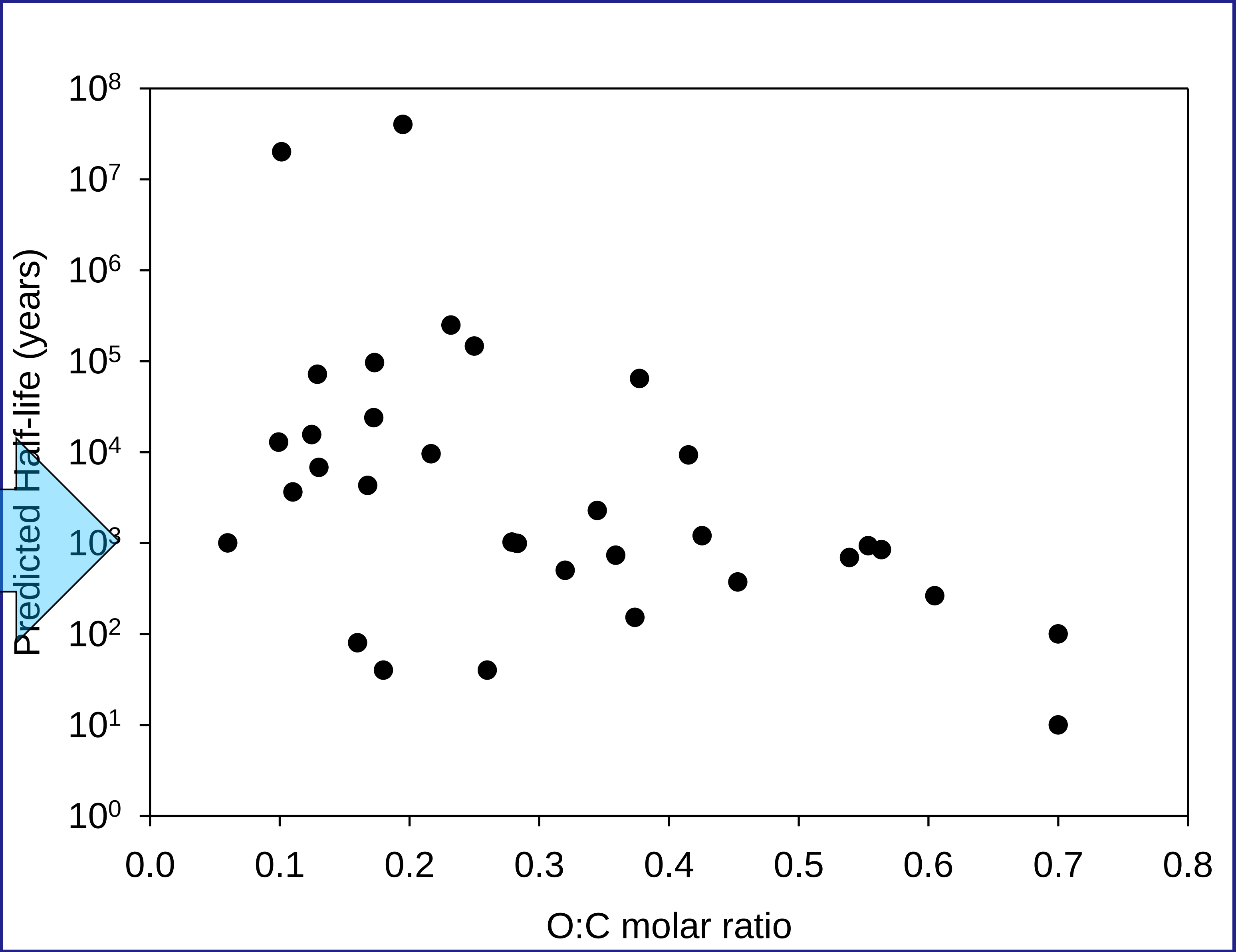

Summary of existing literature studies (n=35) on half-life estimation of biochar [Figure from Spokas (2010)]

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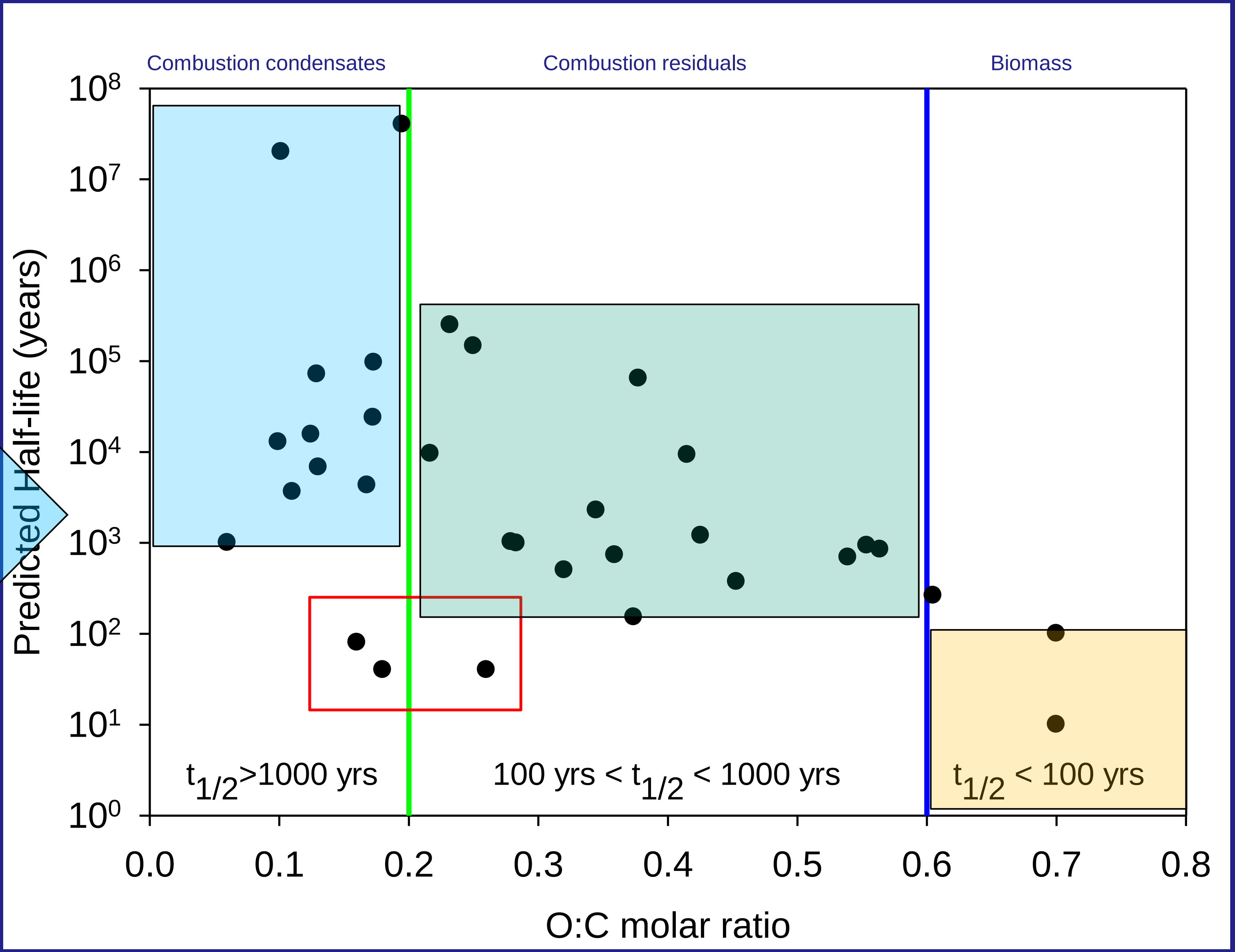
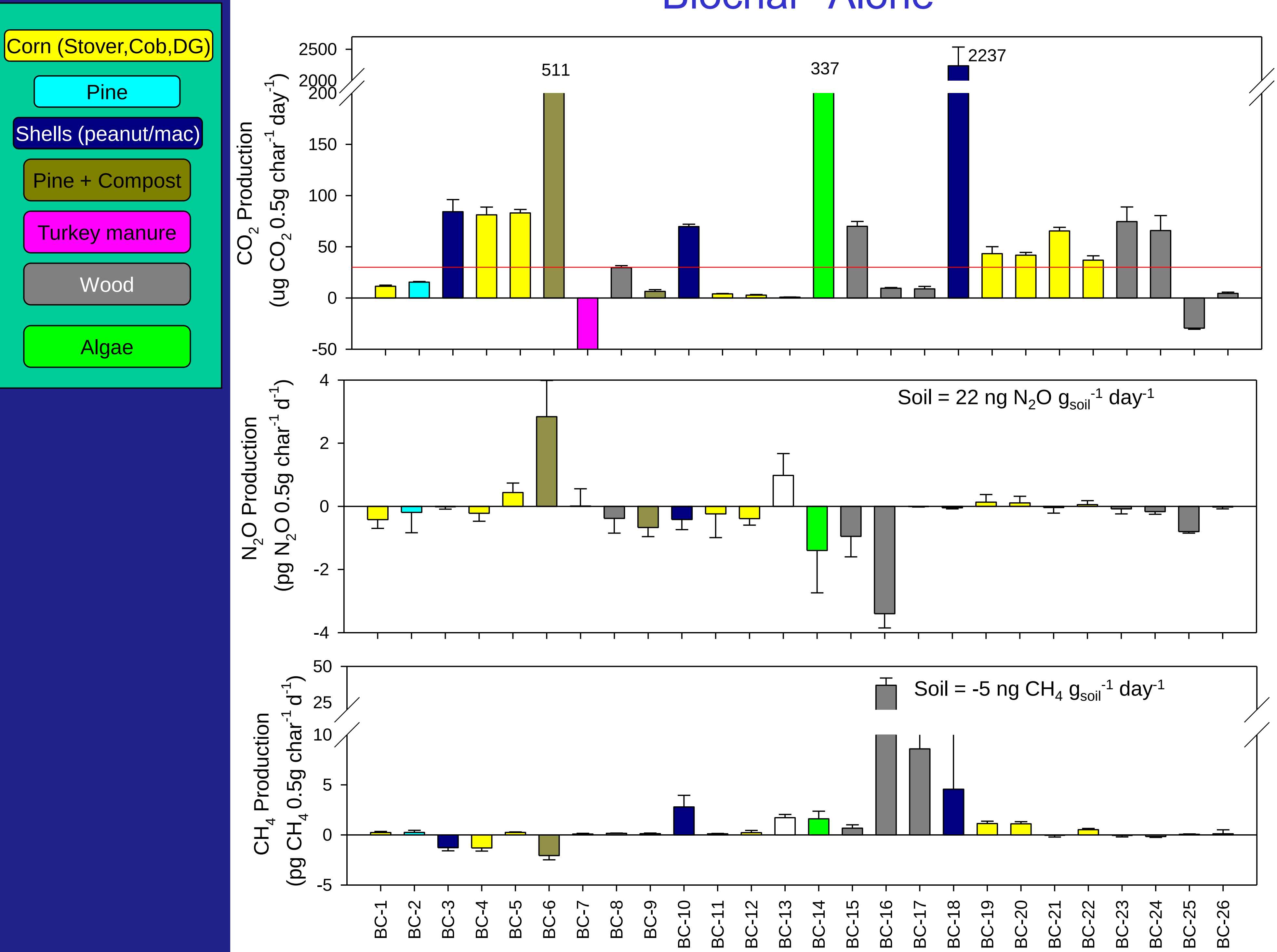


Summary of existing literature studies (n=35) on half-life estimation of biochar [Figure from Spokas (2010)]

Laboratory Biochar Incubations

- Soil incubations:
  - Serum bottle (soil + biochar)
    - 5 g soil mixed with 0.5 g biochar (10% w/w) [GHG production]
    - Field capacity and saturated
  - Mason Jar (biochar mixed & isolated)
    - Looking at impact of biochar without mixing with soil

“Biochar” Alone



Correction for Biochar production

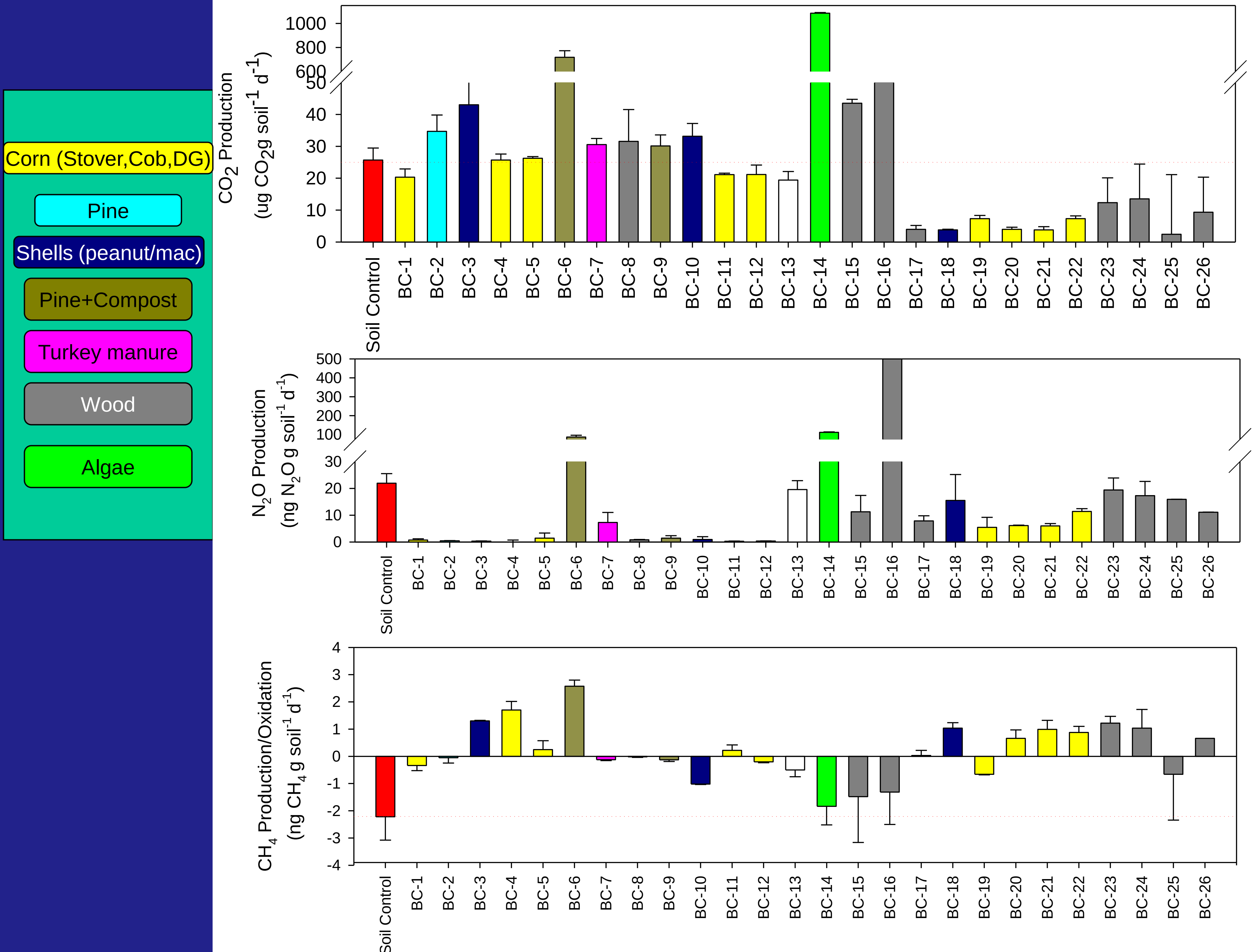
$$\mathrm{CO_2\,Production\ Rate\ Corrrected} = \frac{\left(CO_2^{\,biochar+soil} - CO_2^{\,biochar}\right)}{5g_{soil}(\mathrm{t}_d)},$$

$CO_2^{\,biochar+soil}$ is the total CO_2 production from the soil + biochar + water incubation (µg CO_2) at time t_d

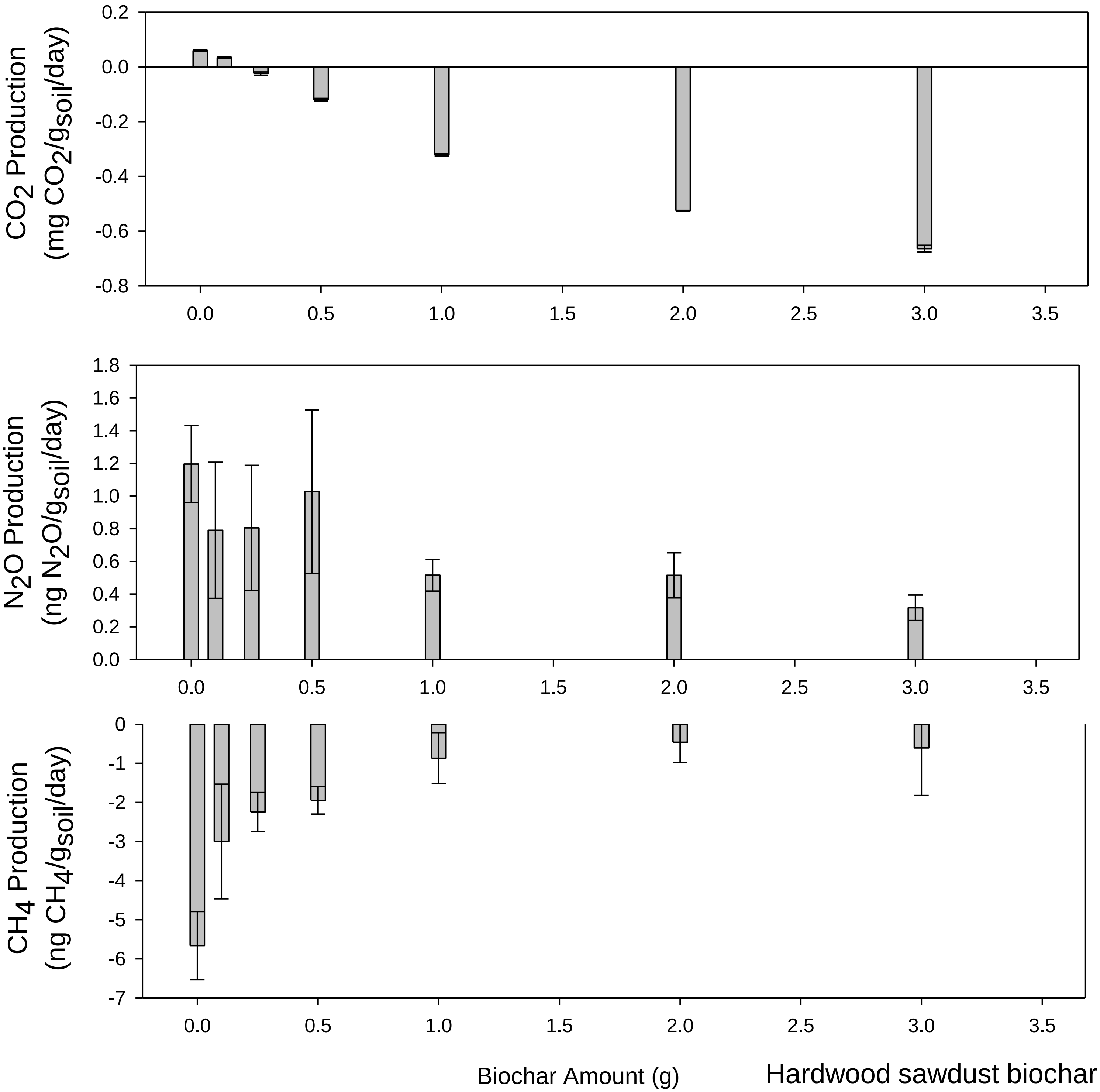
$CO_2^{\,biochar}$ is the total CO_2 production (µg) at time t_d for the biochar + water incubation

t_d is the time of sampling (days)

Soil + Biochar



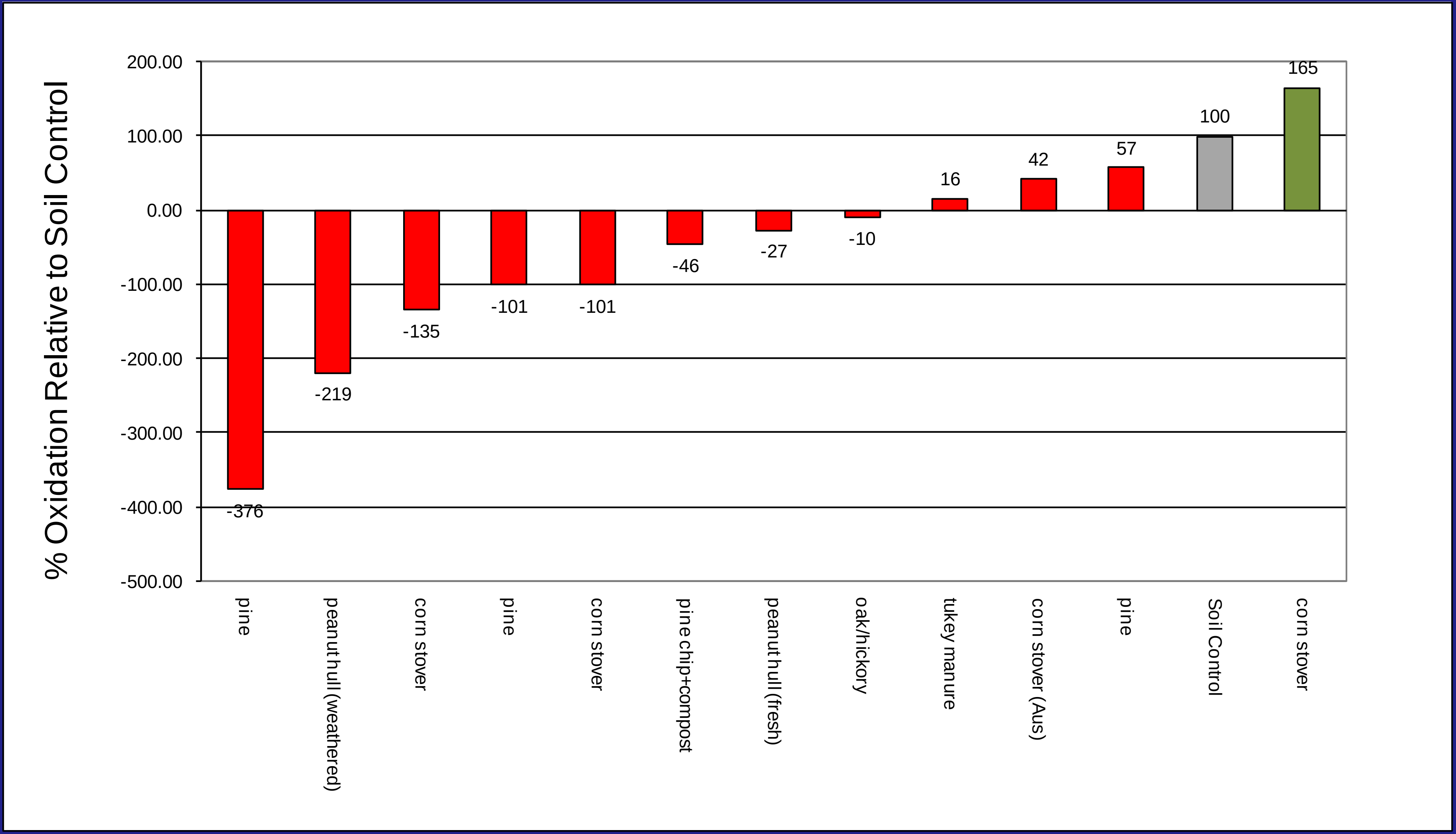
Influence of biochar addition on GHG Production



Hardwood sawdust biochar

Spokas et al., 2009

Ambient CH_4 Oxidation (Agricultural Soil)



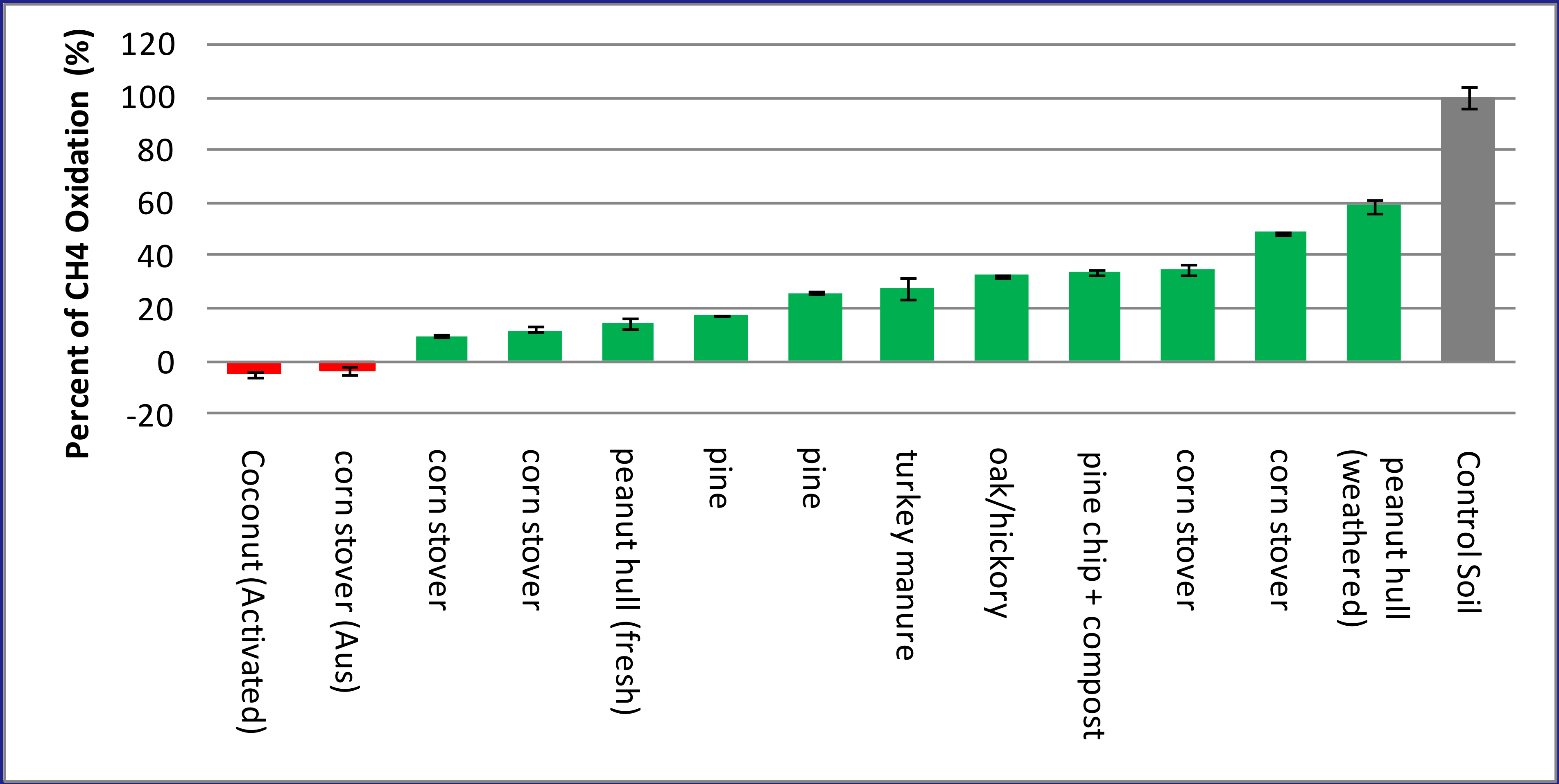
Landfill Cover Soil

- Higher capacity for CH_4 oxidation

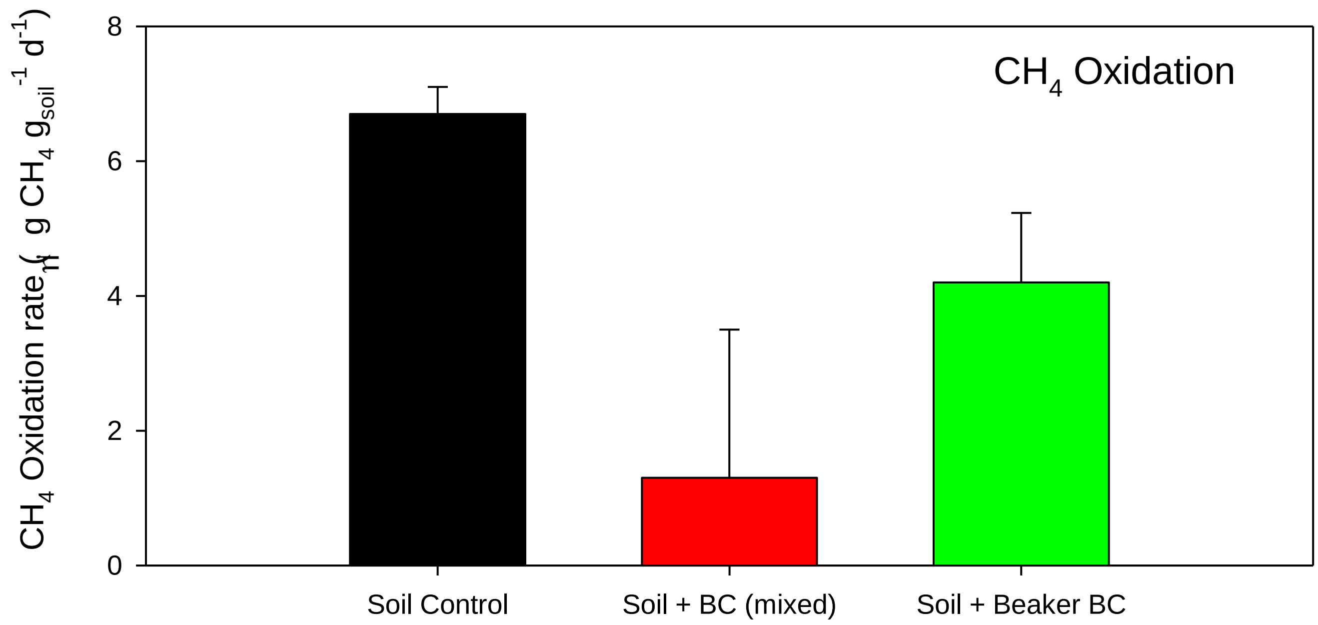
  Easier to assess impacts on CH_4 oxidation effects

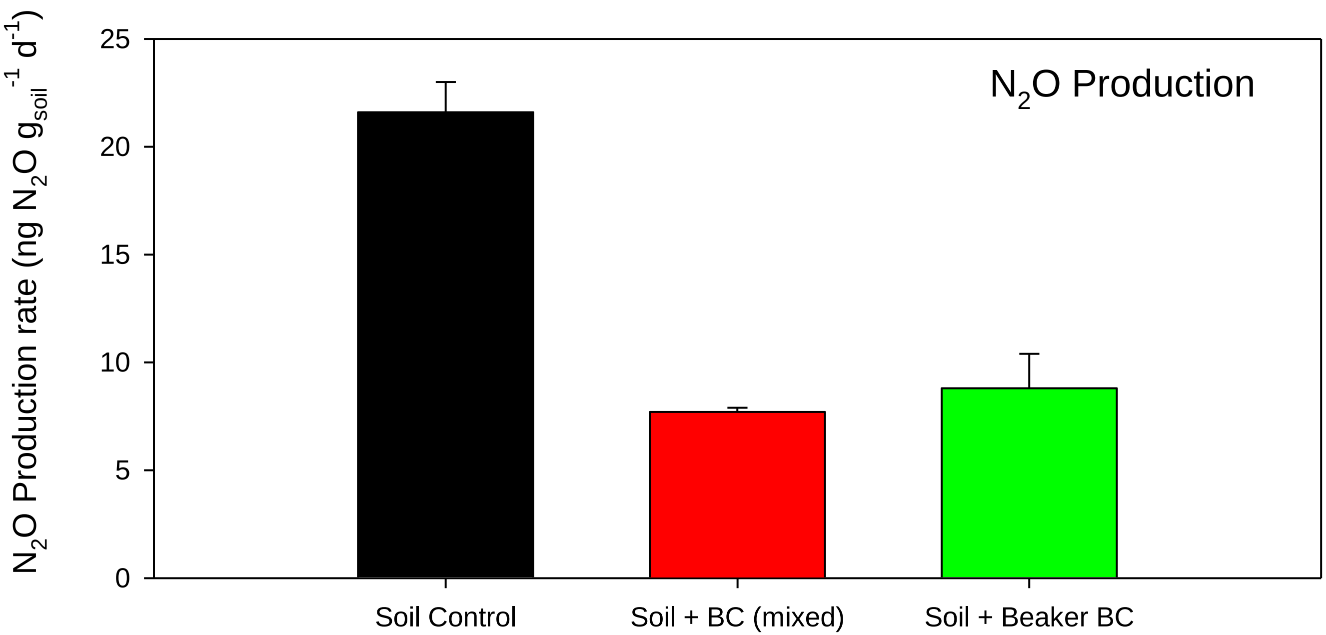
- Large capacity for aerobic N_2O production
  - Composted wood chips/sewage sludge applied to soil

Elevated Levels of CH_4 (1200 ppm)

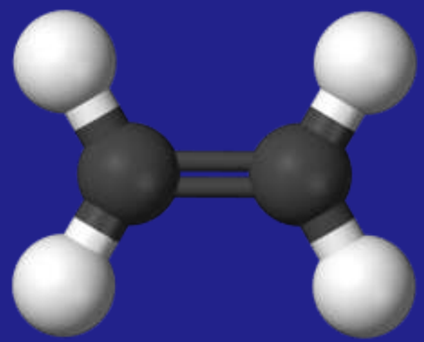


Biochar isolated or mixed with soil

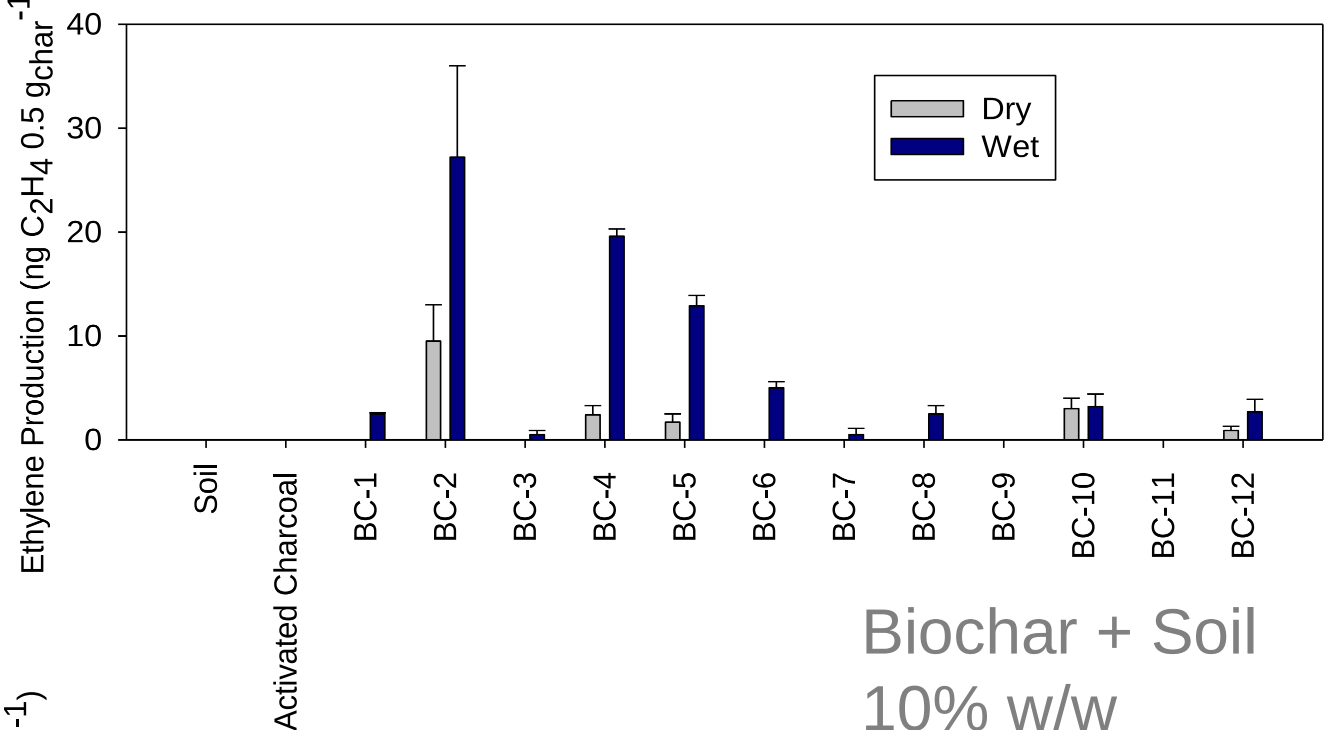




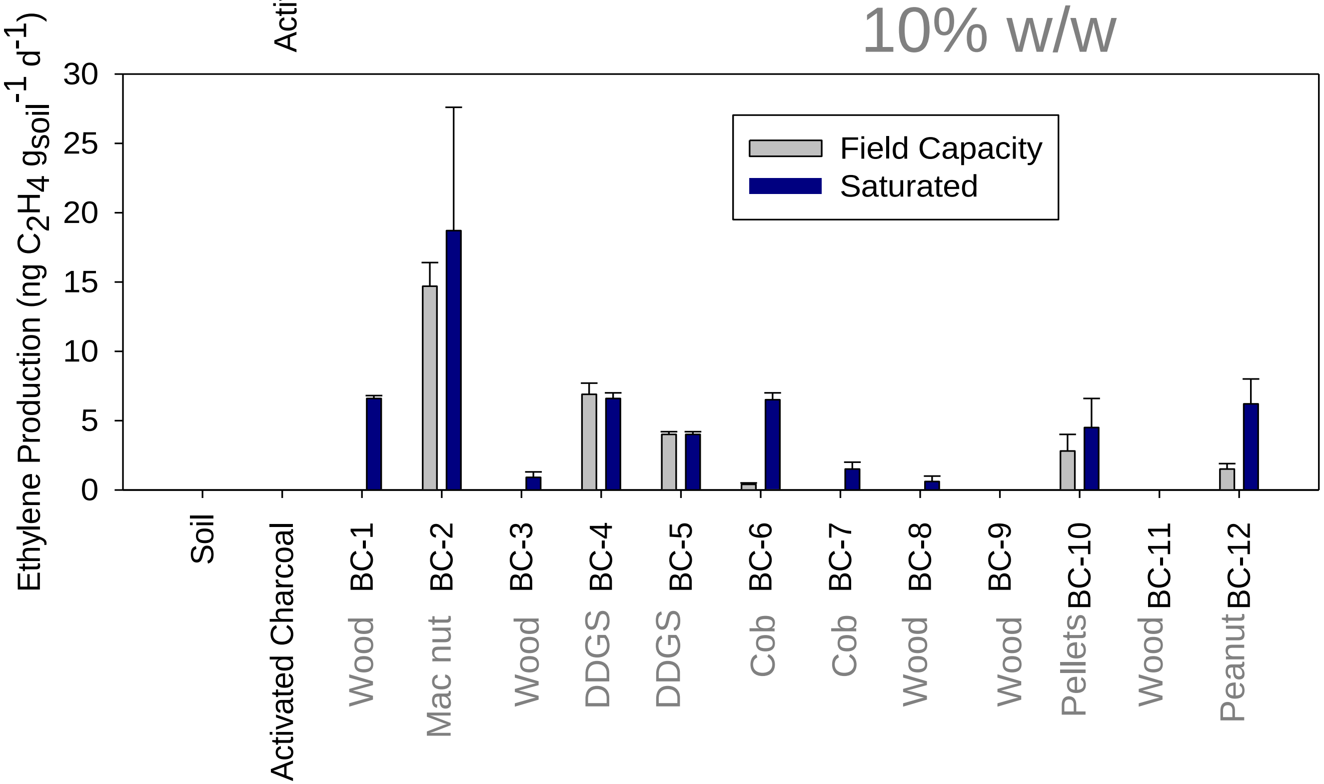
Ethylene (ethene) Production Rates



Biochar Alone



Biochar + Soil 10% w/w

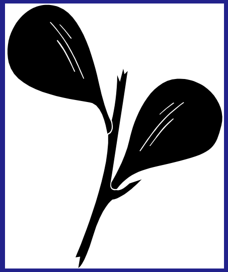


Ethylene

Long History

Ancient Egyptians: Fig ripening

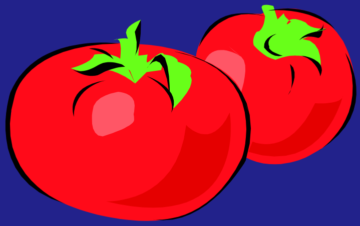
Chinese: Pear ripening



1800's gas leaks around street lights : vegetation response

1901 responses linked to ethylene presence

Activated charcoal added to shipping containers to sorb ethylene and reduce fruit ripening

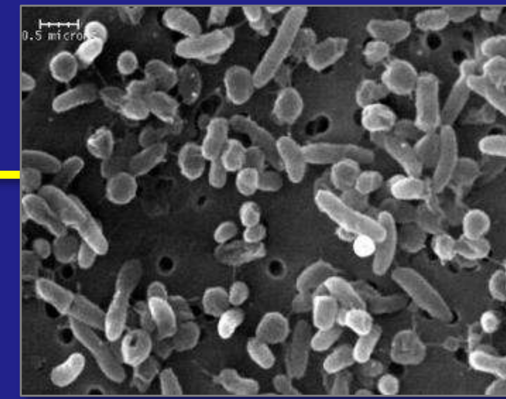


Ethylene used to stimulate ripening

Bananas, tomatoes

- Most abundant human produced organic compound

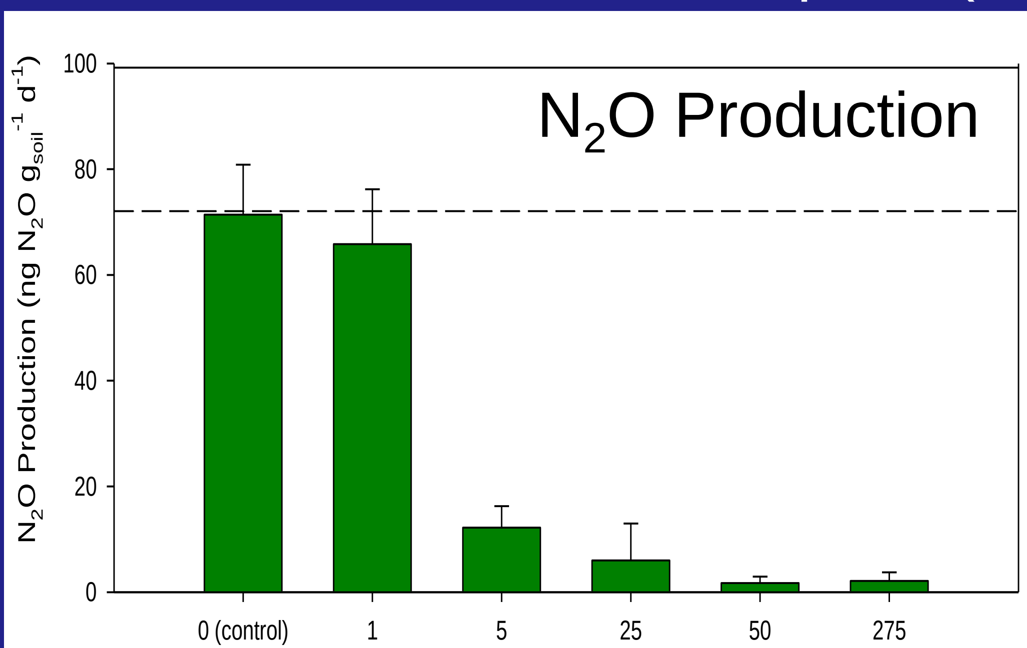
Ethylene Impacts



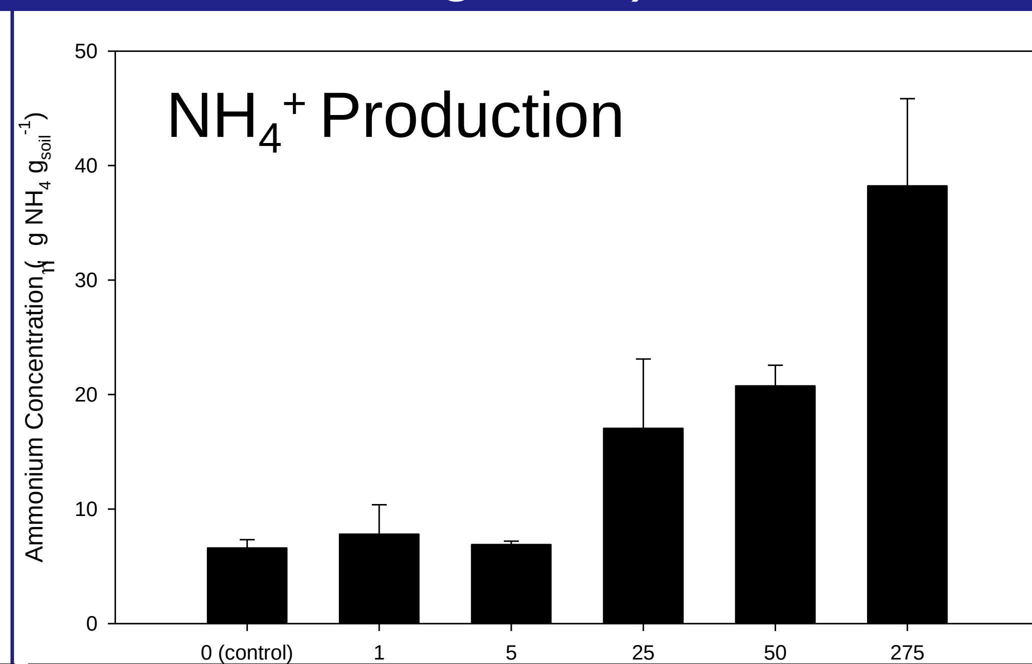
Soil Microbial Impacts

- ✓Induces fungal spore germination
- ✓Inhibits/reduces rates of nitrification/denitrification
- ✓Inhibits CH_4 oxidation (methanotrophs)
- ✓Involved in the flooded soil feedback

  Both microbial and plant (adventitious root growth)



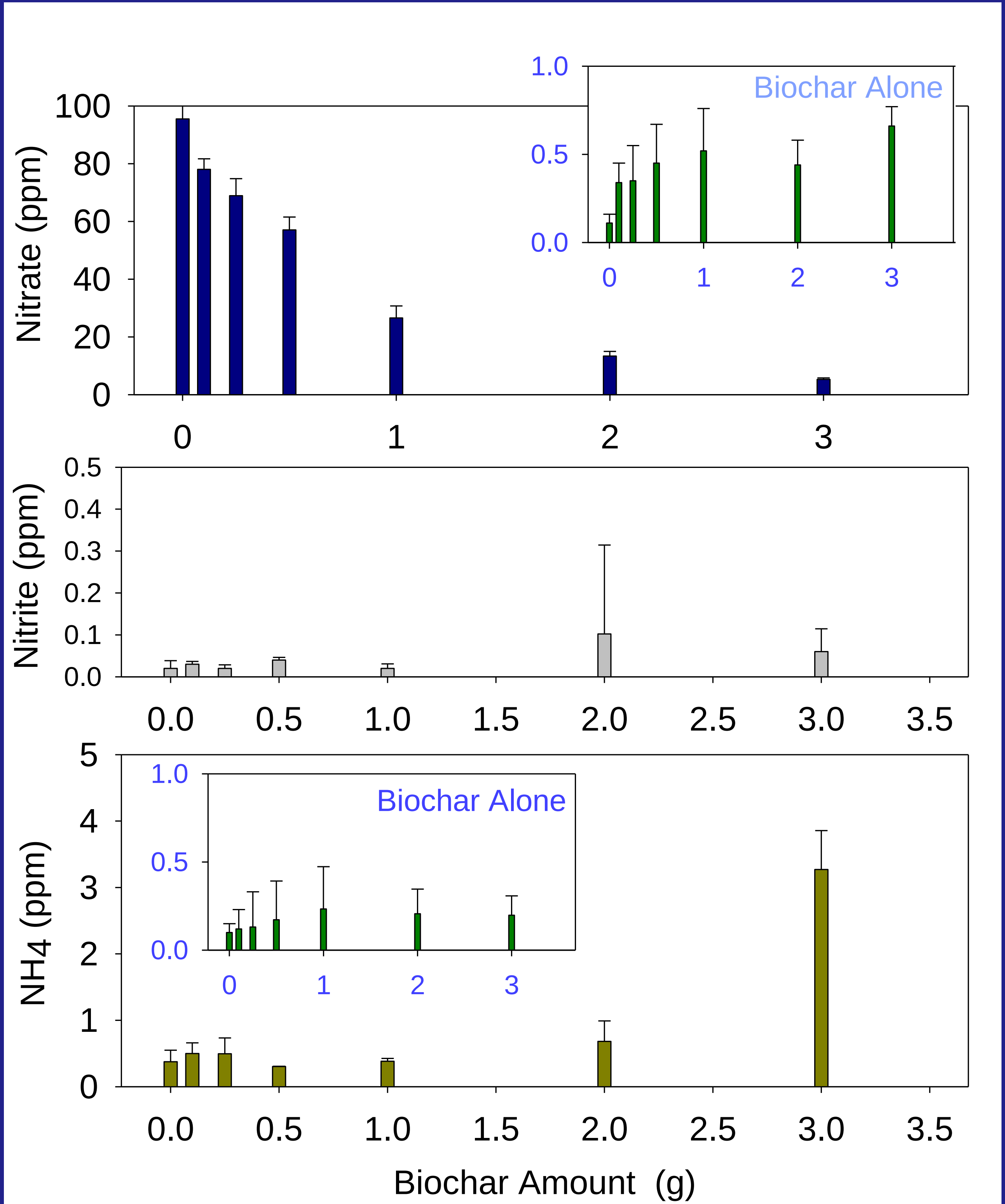
Ethylene Headspace Concentration (0 to 275 ppmv)



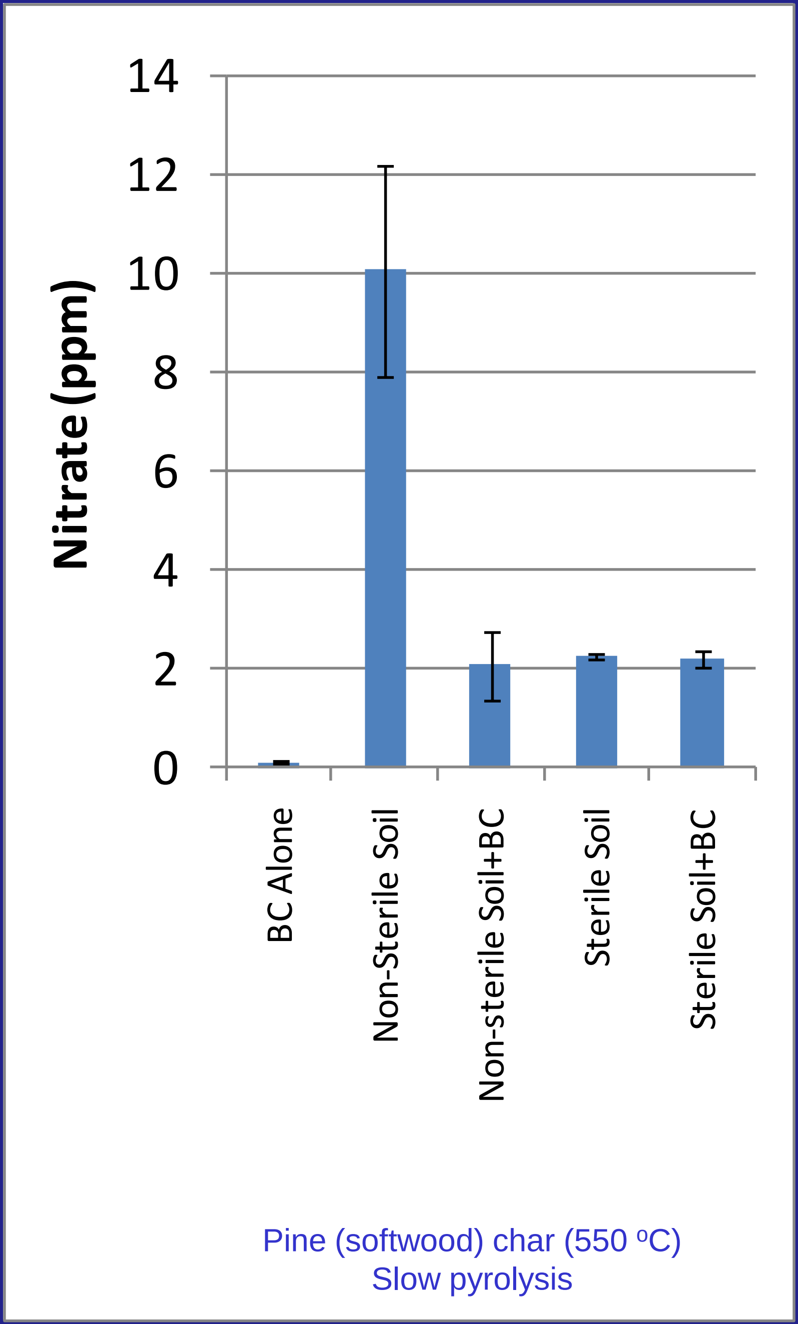
Ethylene Headspace Concentration (0 to 275 ppmv)

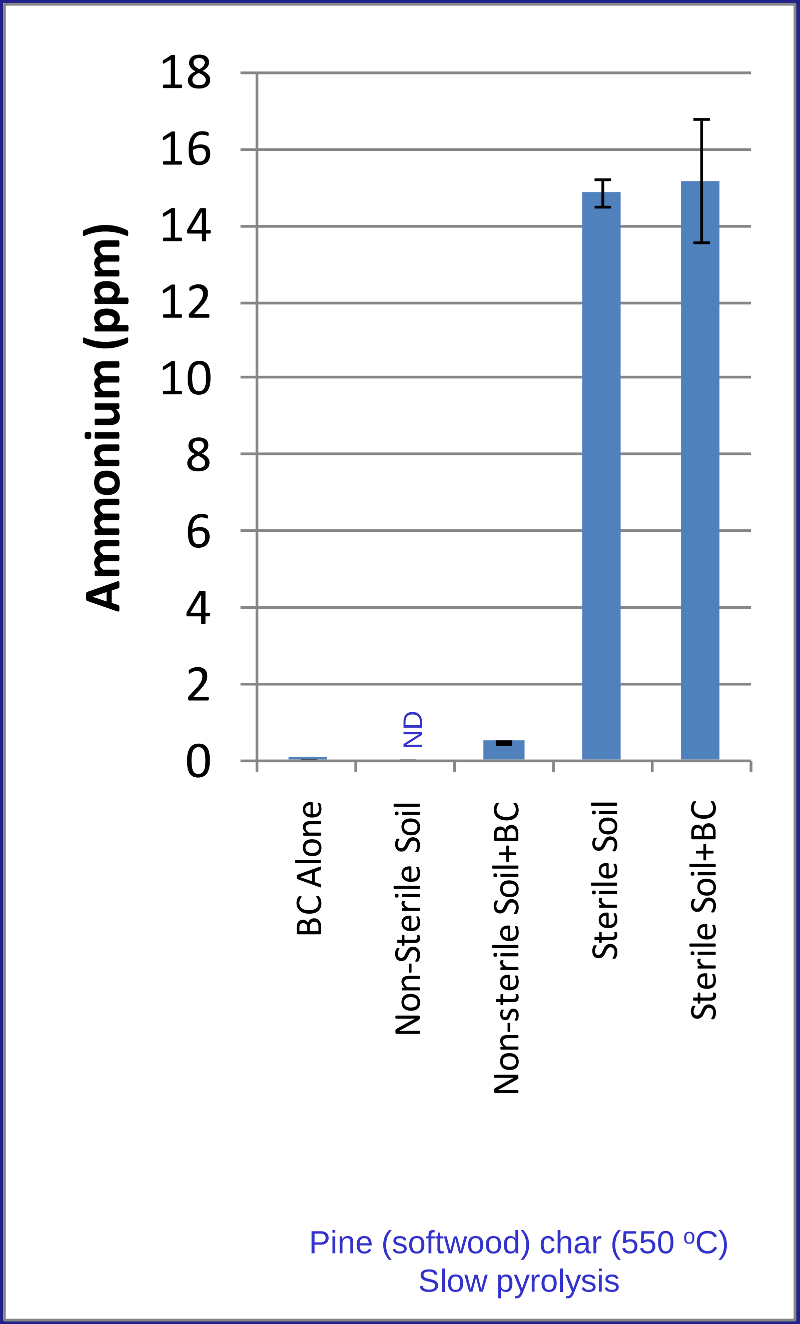
Closer look at N-cycling

(hardwood sawdust biochar)

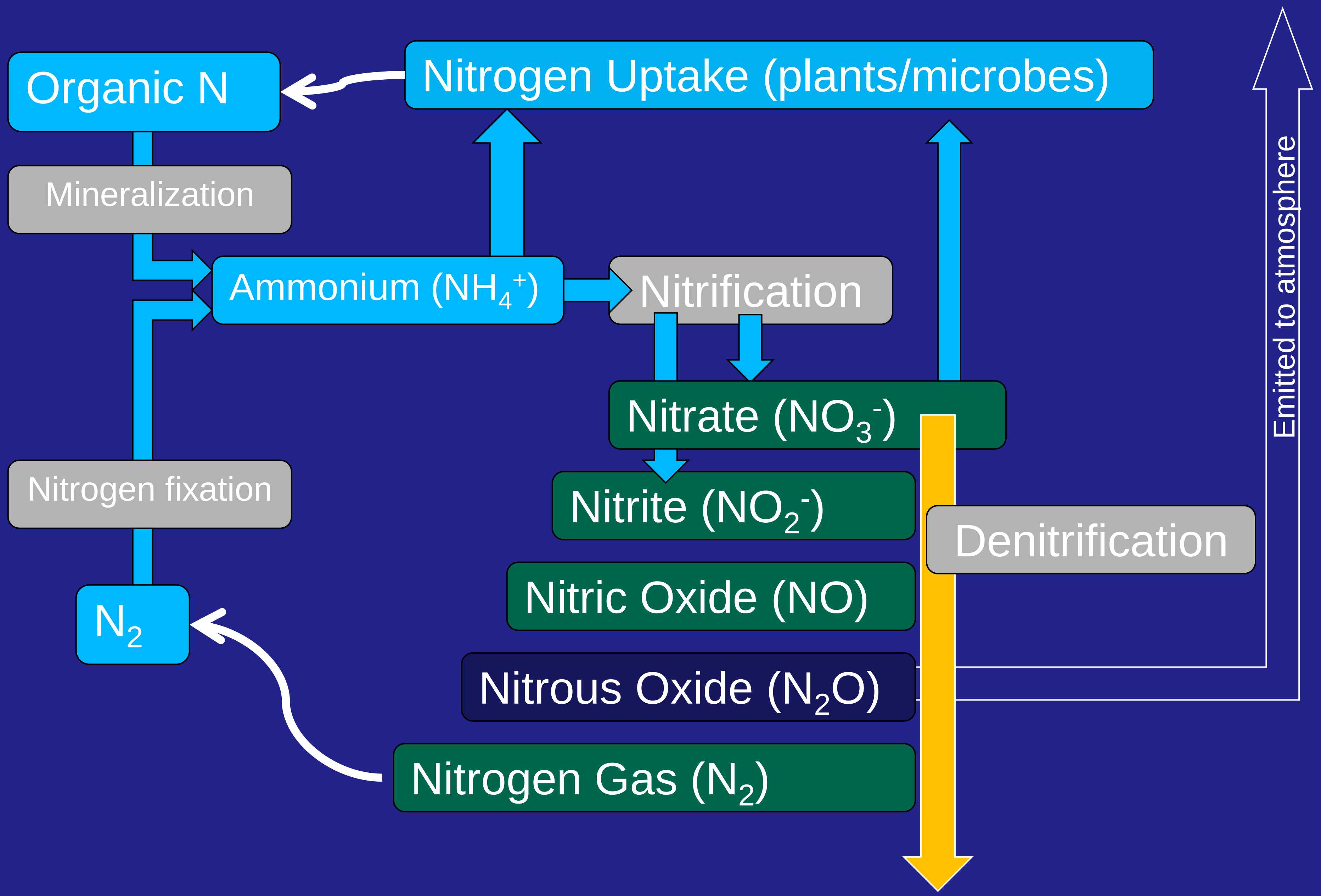


N-cycling: Sterilized soil + biochar

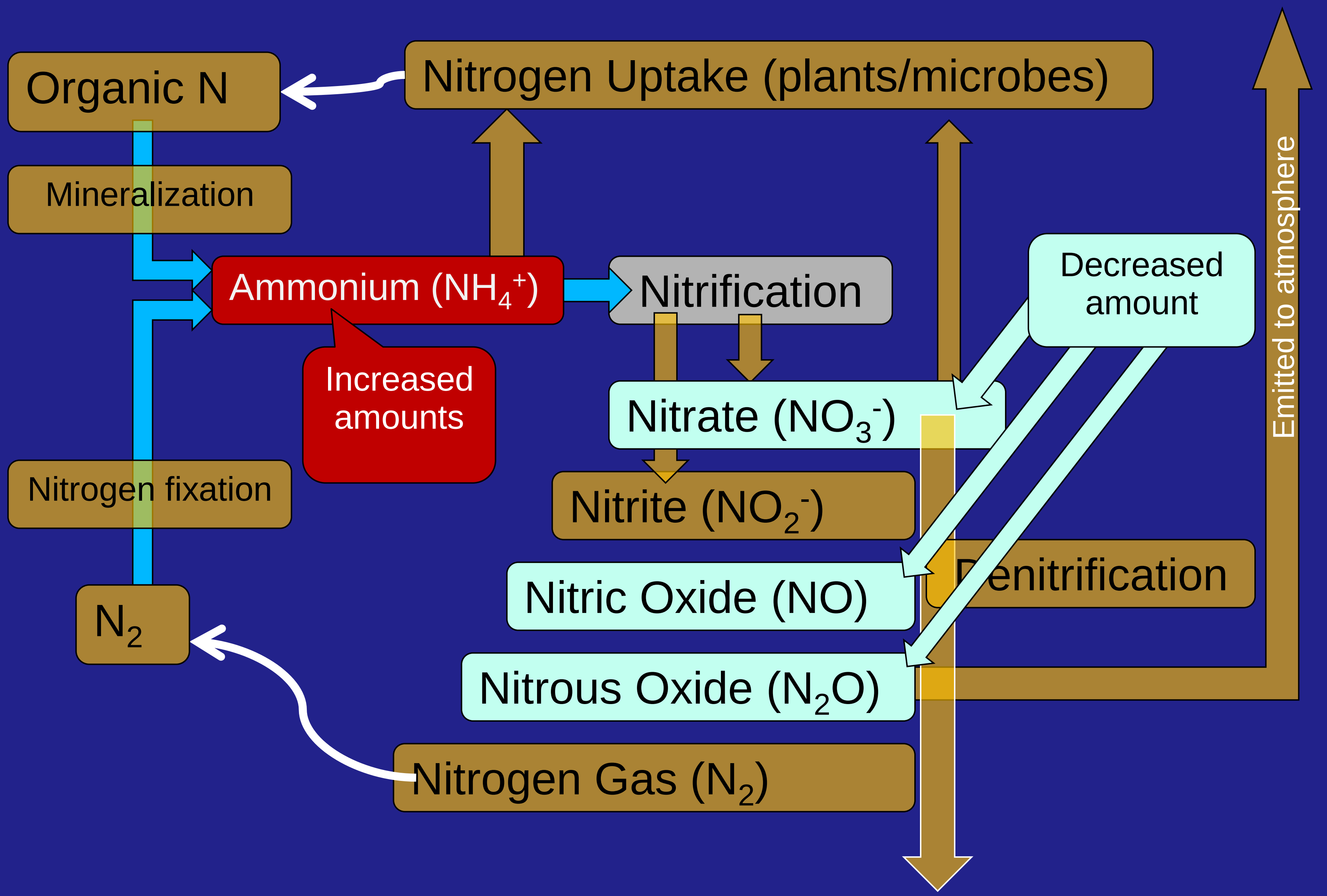




Brief Overview of N-cycle



Putting the pieces together: Not quite a full picture yet…



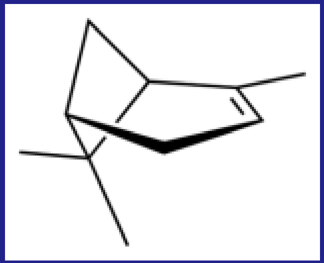
Ethylene Production

•Ethylene could provide a mechanism behind reduced nitrification/denitrification activity

•Could also be important in plant responses as well

•Clough et al. (2010) also hypothesized that **α-pinene** could be involved as a nitrification inhibitor

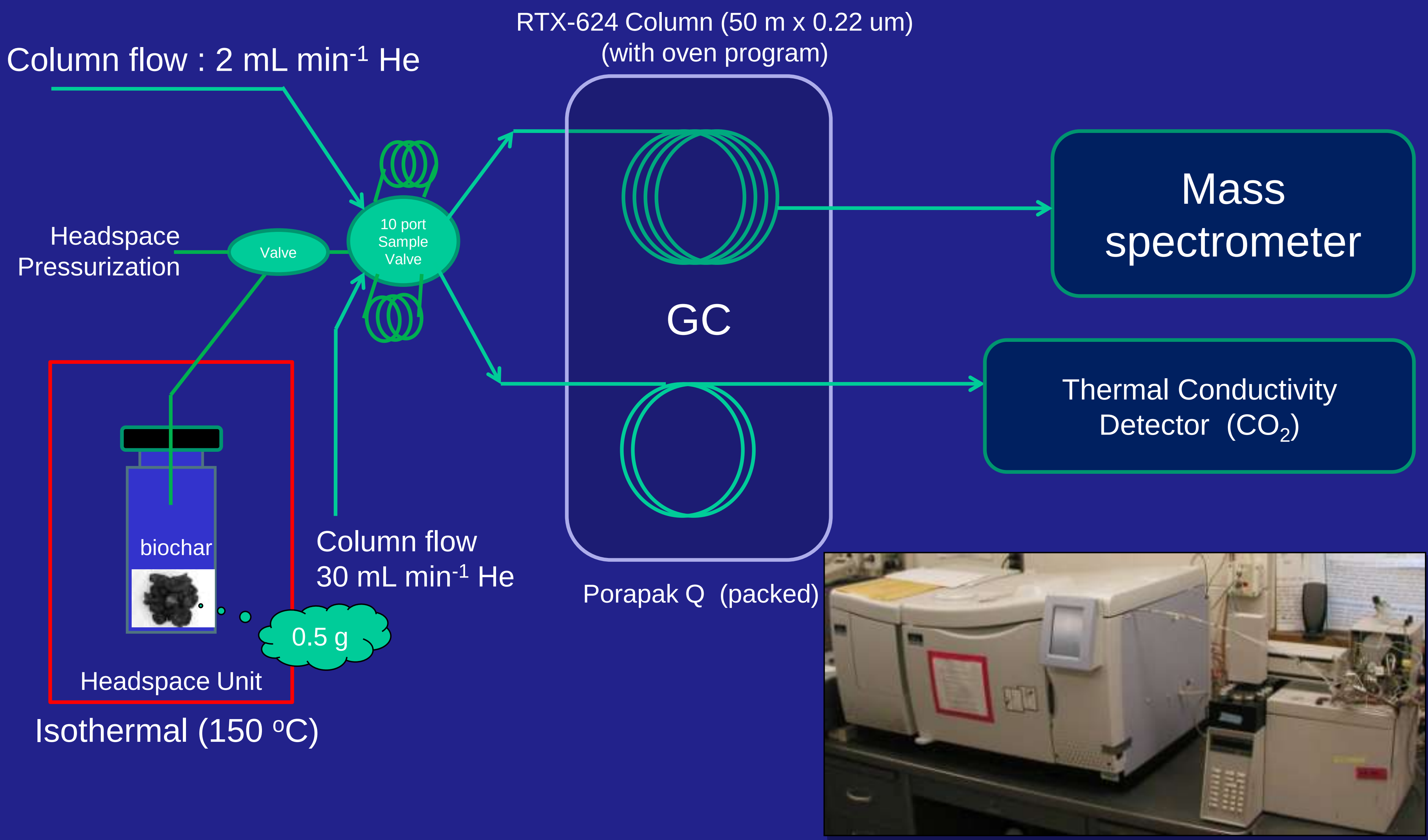
- α-pinene observed as volatile from vegetation
- involved in insects' chemical communication system



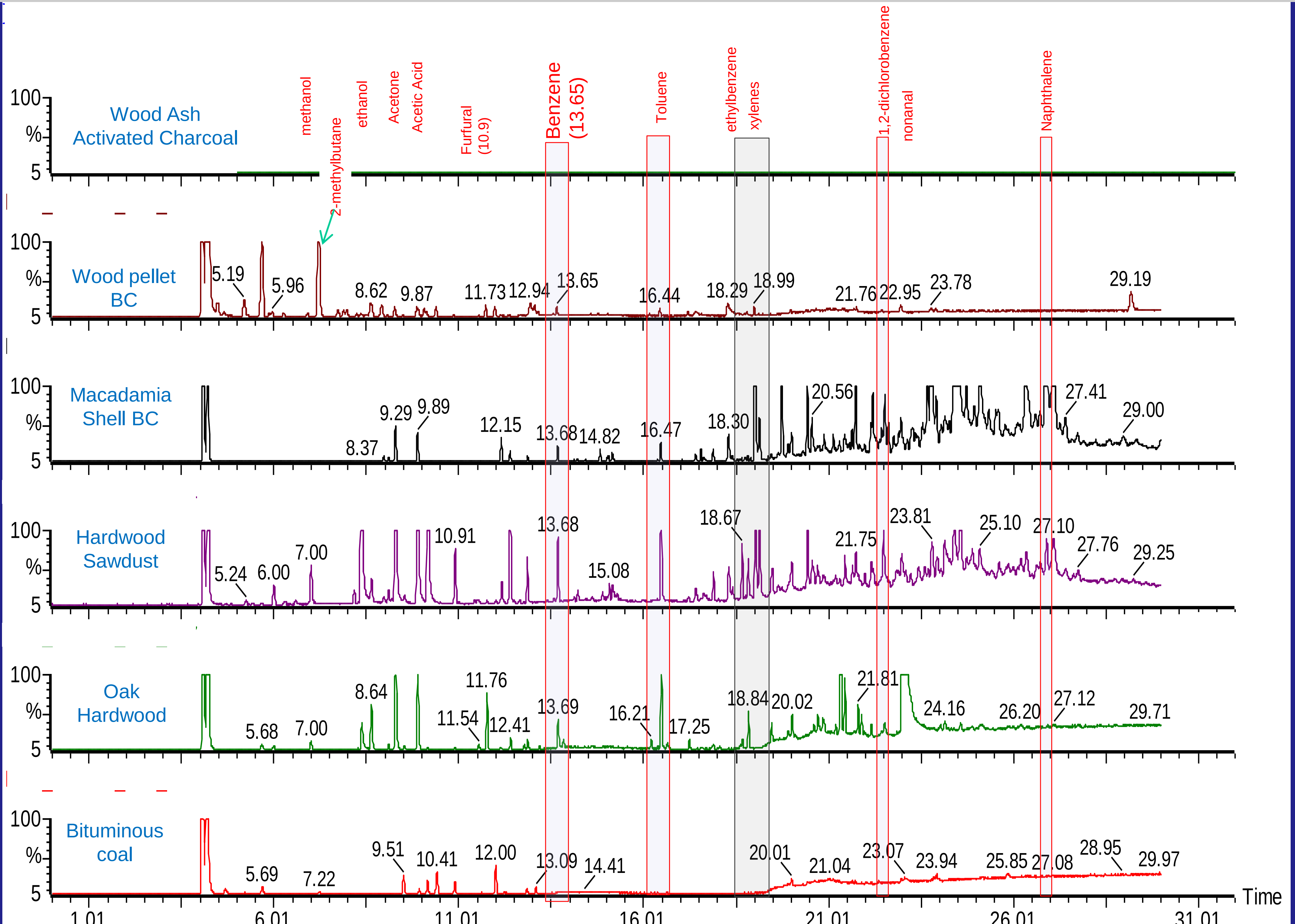
•Despite the different chemicals – Same mechanism:

Chemical inhibitors behind the suppression of N_2O production

Headspace Thermal Desorption-Mass Spectrometry

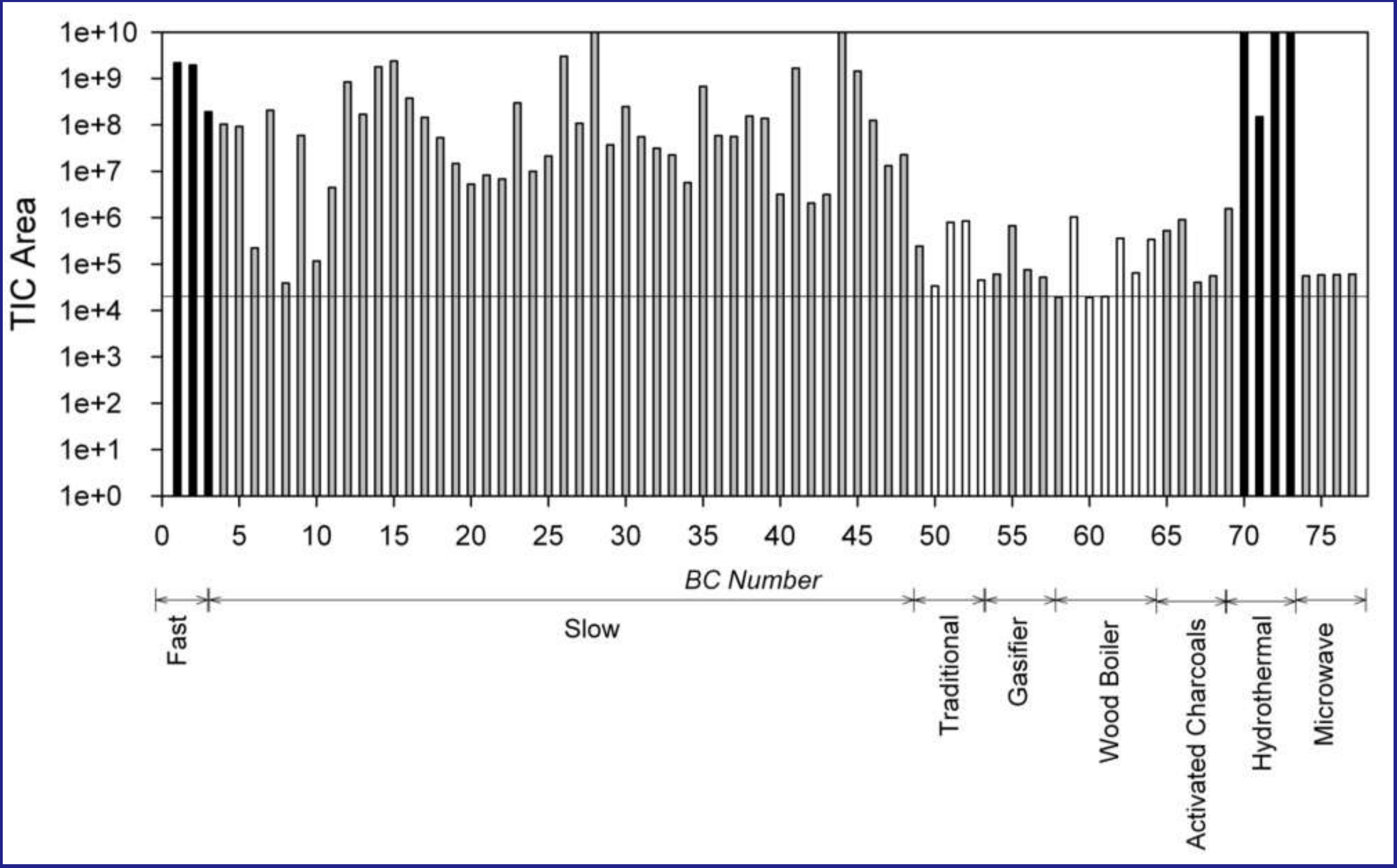


Headspace Thermal Desorption GC/MS scans of biochars



Biochar has a variety of sorbed volatiles = range of potential microbial inhibitors

Distribution of Sorbed Organics



Spokas et al. 2011

Biochar: Sorbed Organics Impacts

Deenik et al. (2010):

Negative plant growth effects as a consequence of high VM biochar

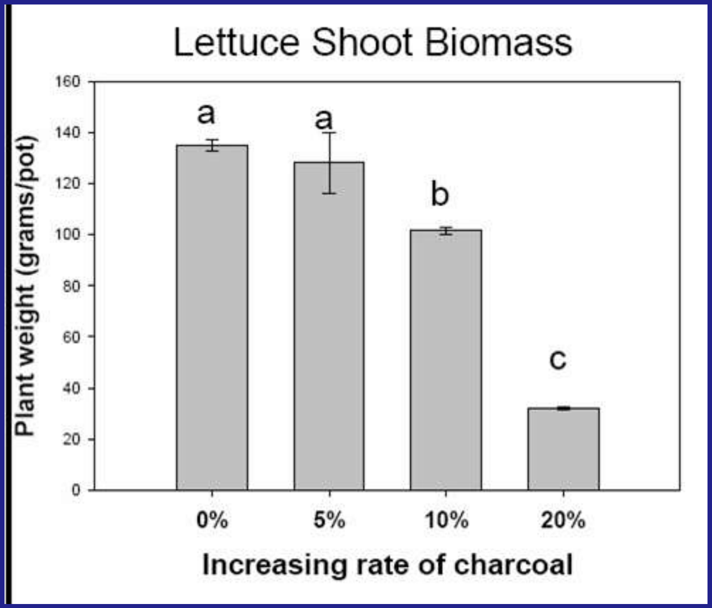


Figure from Deenik et al. (2010)

Zimmerman (2010) :

VM potential indicator variable for biochar stability estimations

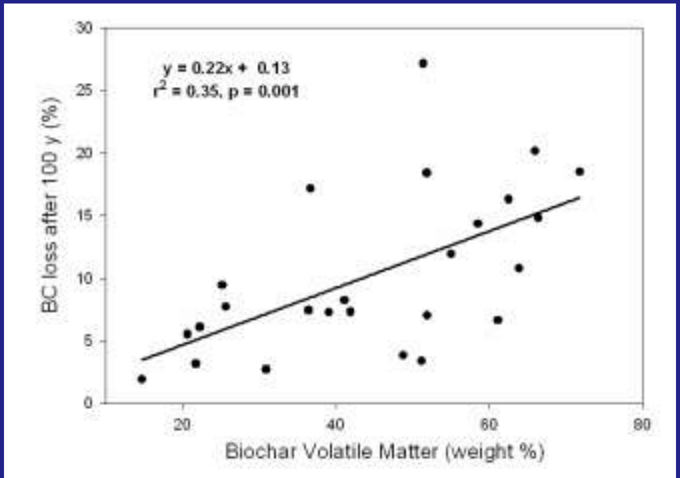
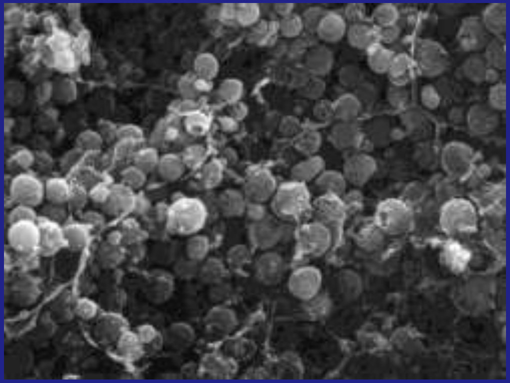


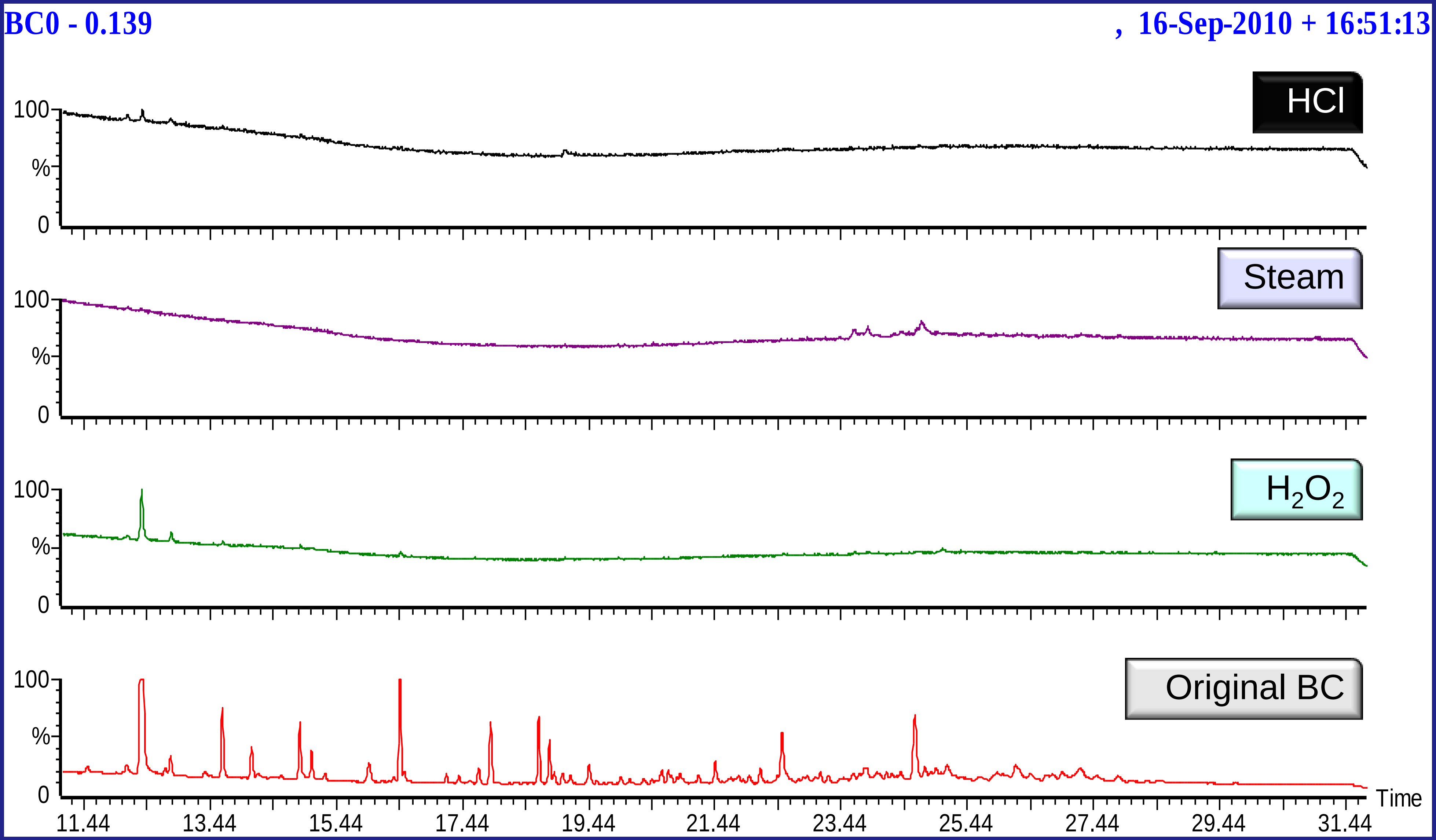
Figure from Zimmerman et al. (2010)

Impact of Biochar Volatiles in Soils

- Volatile organic compounds can interfere with microbial processes
  - Terpenoids – interfere with nitrification [Amaral et al., 1998; White 1994]
  - Furfural + derivatives – inhibits microbial fermentation & nitrification (Couallier et al., 2006; Datta et al. 2001)
  - Benzene, Esters – Also inhibit microbial reactions
  - Still ongoing and developing research area in the plant/microbe research area
- Alterations in VOC content could be sensitive indicators of soil conditions (Leff and Fierer, 2008)
- Sorbed biochar volatiles could interfere with microbial signaling
  - Release or sorb signaling compounds



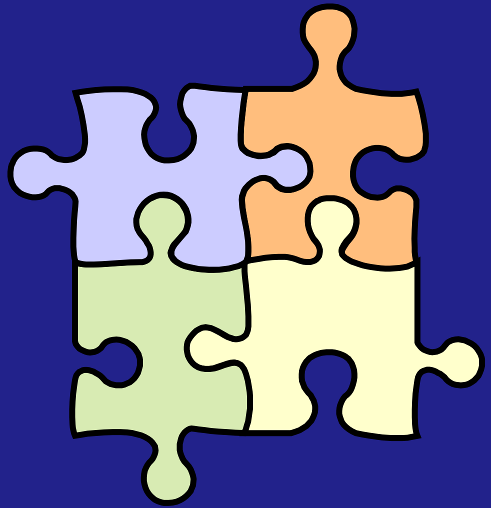
Activation Effect on VOC Content



Conclusions

- Biochar is not a new material – new purpose
- Another piece to the puzzle: Ethylene + sorbed VOC's
  - Sorbed volatiles and degradation products (ethylene) should be included in the potential biochar mechanisms
  - Microbial inhibitors – Could also explain plant effects
- Reduction in N_2O production : Consequence of sorbed volatiles impacting the nitrification process (?)
  - Accumulation of NH^+_4 and decreased NO^-_3 production
  - Length of impact ?
- No absolute "biochar" consistent trends: Highly variable and different responses to biochar as a function of soil ecosystem (microbial linkage) & position on black carbon continuum:

  Typically:
  - Reduced basal CO_2 respiration
  - Reduced CH_4 oxidation activity
  - Reduced N_2O production activity (except for higher N)
  - Reduced NO_3 production
  - Increased extractable NH_4 concentrations
  - Exceptions DO exist



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    - National Council for Air and Stream Improvement (NCASI)
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    - Chip Energy
    - AECOM
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Thank-you for your attention

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