BIOCHAR: REACTIONS WITH DISSOLVED NITRATE AND AMMONIA

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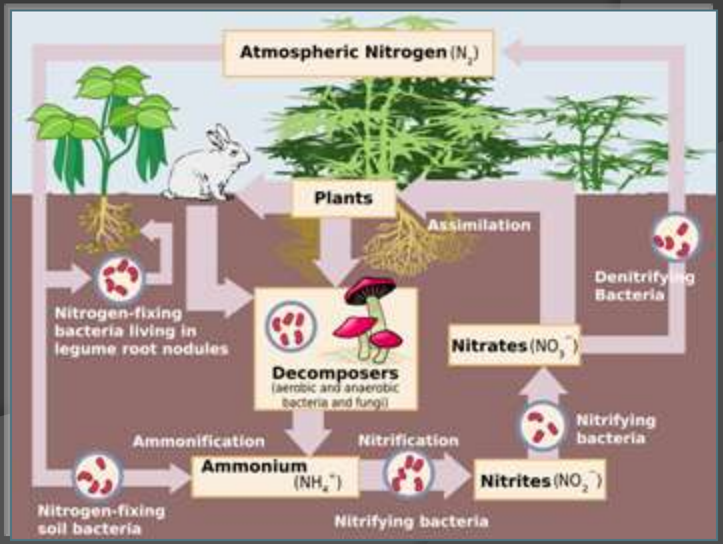
USDA

Objectives

- To assess the potential interaction of biochar with dissolved ammonium (NH_4^+) and nitrate (NO_3^-)
  - Why?
    - Sorption of NH_4^+ and NO_3^- to biochar has been cited as a possible mechanism for the suppression of soil N_2O production & NO_3 leaching



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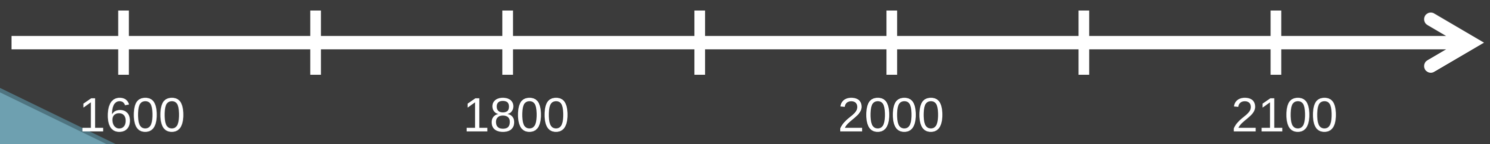
    - Sorption of NH_4^+ and NO_3^- to biochar have been cited as a possible mechanism for the suppression of soil N_2O production & NO_3 leaching
    - Potential use biochar for nitrate remediation efforts
      - Tile drains, contaminated groundwater, etc.

History: Charcoal + Inorganic N



2000 BC

Romans used charcoal as a water filtering media

History: Charcoal + Inorganic N

1600 1800 2000 2100

1791

Lowitz - First documented scientific evidence that charcoal “decolors” solutions

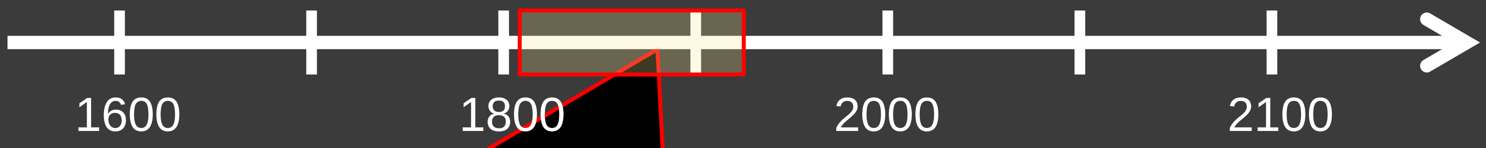
History: Charcoal + Inorganic N

Gunpowder Years (1810 – 1920's)

Major emphasis of scientific efforts
➔ Improving gunpowder

Optimization of the reaction of charcoal with inorganic N-forms (nitrate).

History: Charcoal + Inorganic N



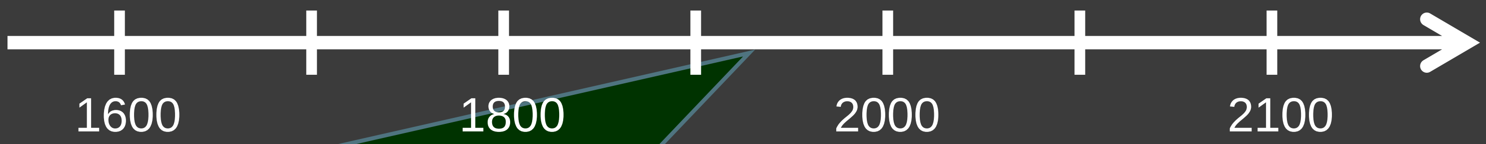
Munroe (1885) :

"*Gunpowder is such a nervous and sensitive spirit, that in almost every process of manufacture; it changes under our hands as the weather changes.*"

- **Pressing times of charcoal varied with the relative humidity**

"Notes on the literature of explosives no. VIII"
Proceedings of the US Naval Institute, no. XI, p. 285

History: Charcoal + Inorganic N



1917 - USDA

> Examined multiple species of trees

> *Pacific Willow* = best for gunpowder production (400-450 ^{o}C)

$$6\ KNO_3 + \underbrace{C_7H_4O}_{\text{Charcoal}} \longrightarrow 3\ K_2CO_3 + CO_2 + 6\ CO + 2\ H_2O + 2\ N_2$$

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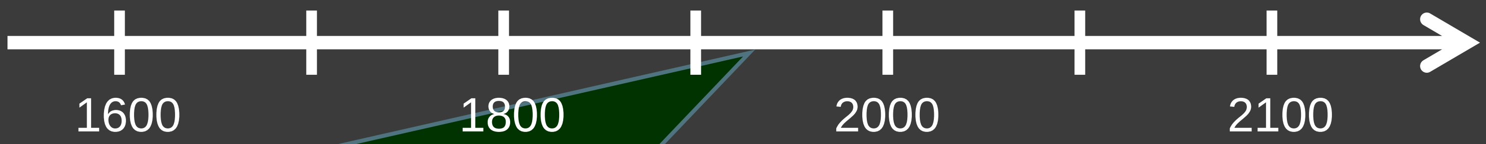

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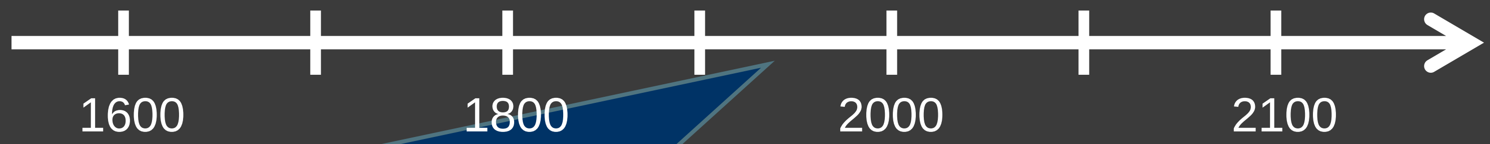
Pathway for *Nitrate* → *N_2* gas directly (outside of typical soil microbial N-cycle)

History: Charcoal + Inorganic N



1920-1960

- Focus on use of charcoal in analytical methodology
  - Observed disappearance of N-forms (interference)

[e.g., Harper 1924; Burrell and Phillips 1925; Gibson and Nutman 1960; Scholl et al. 1974]

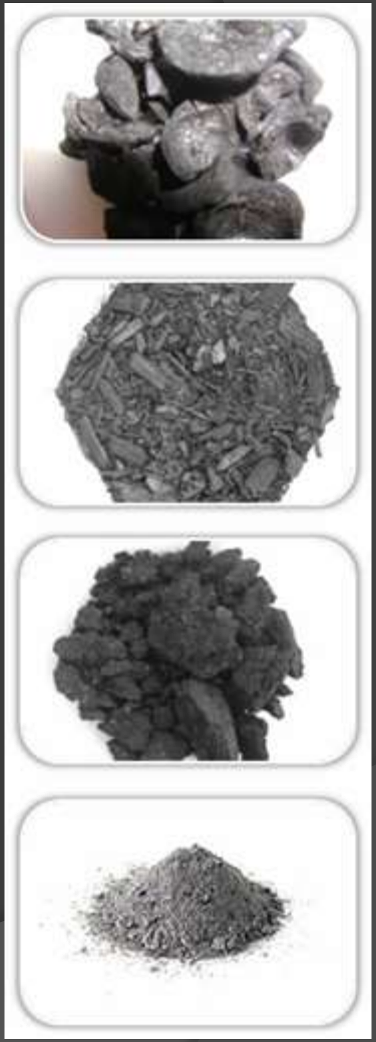
Overall conclusion:

Charcoal was sorbing the nitrate, nitrate, and/or ammonia

** But not all charcoal sorbed equally

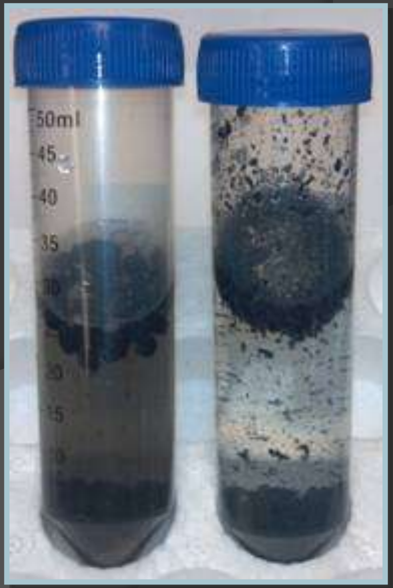
Biochars Examined

- 35 different biochars
- 28 different pyrolysis units
  - Laboratory scale
  - Entrepreneur scale (homemade units)
  - Pilot scale
  - Small industrial scale units (tons/day)
  - Wood fired boilers (high C wood ash)

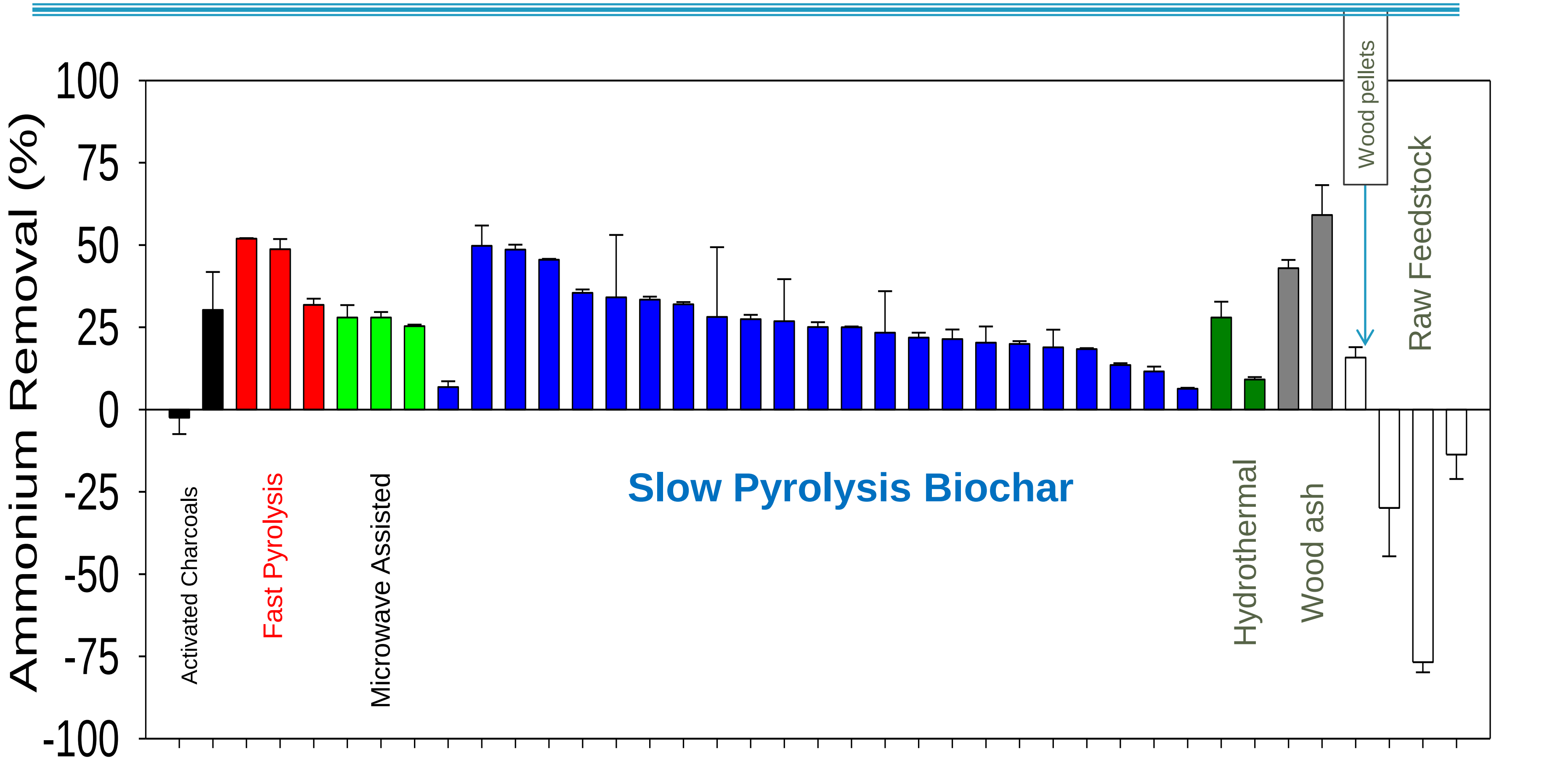


Experimental Design

- Batch equilibrium
  - 20 ppm NH_4^+ and 20 ppm NO_3^-
  - Limited number of biochars: Sorption isotherms
  - Triplicate replicates
  - Used ^{15}N labeled N-forms
    - Samples not analyzed

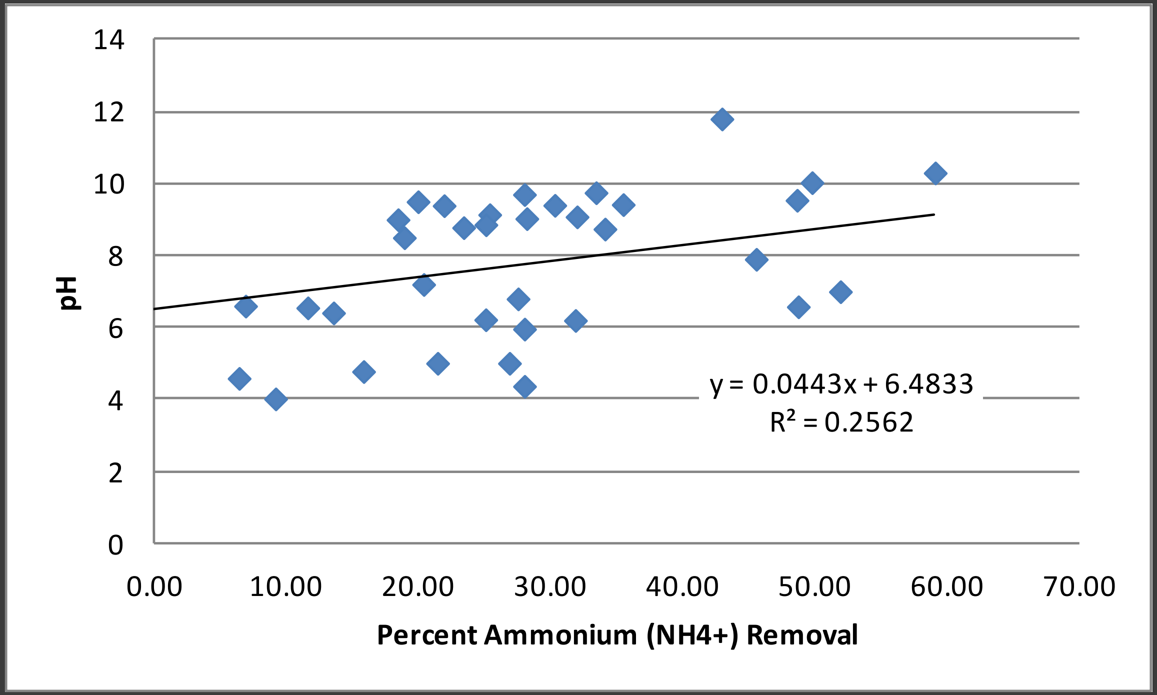


Ammonium removal



- Activated charcoals: -2.5% to 30% removal
- Range of removal efficiencies: Biochar : 5 – 60%
- No significant differences observed between types

pH Effects

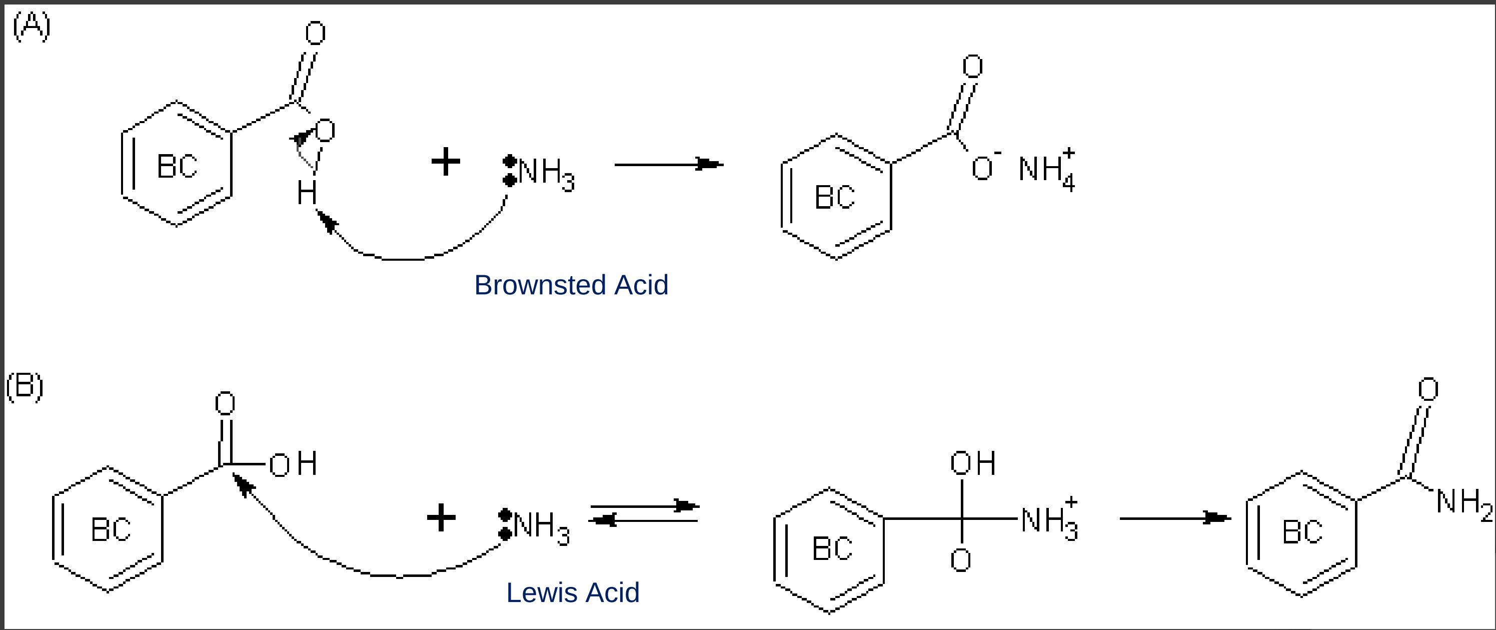


- No statistically significant relationships

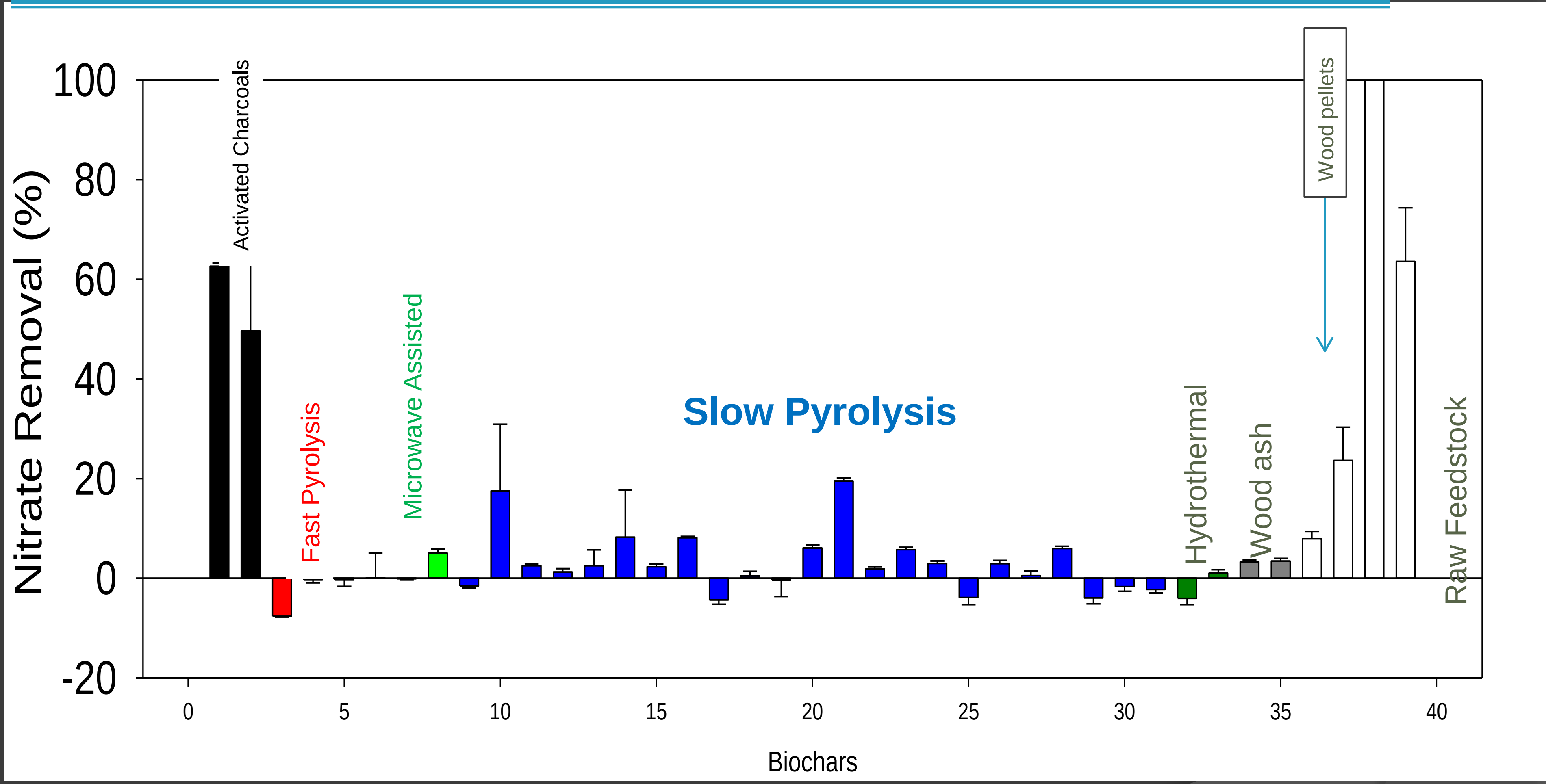
- Majority of the solutions were alkaline :
  Ammonia volatilization losses?

Ammonia reaction with Biochar

- The ability of black carbon to react with ammonia has been known for some time (Holmes and Beebe 1957)

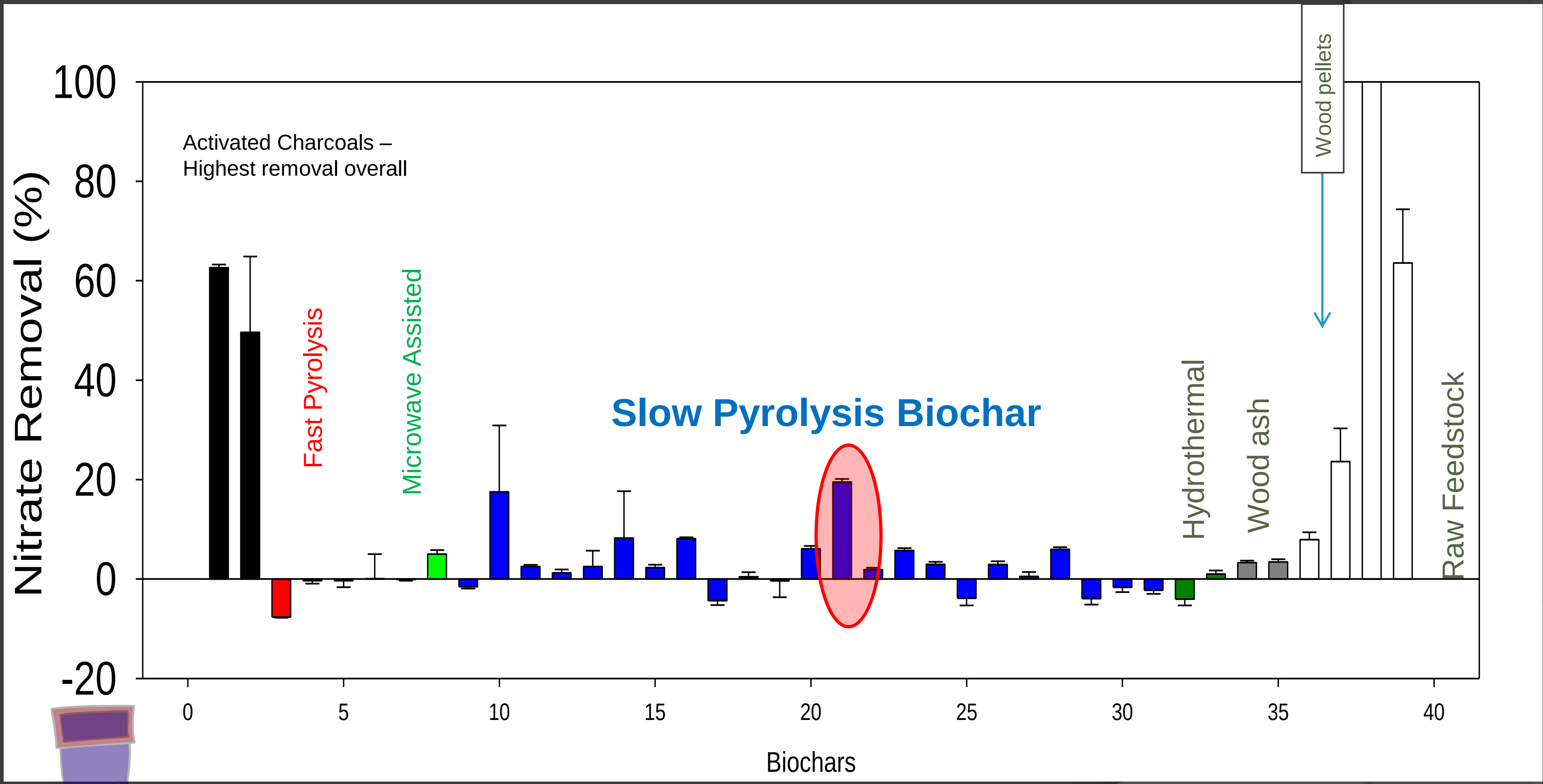


Nitrate removal



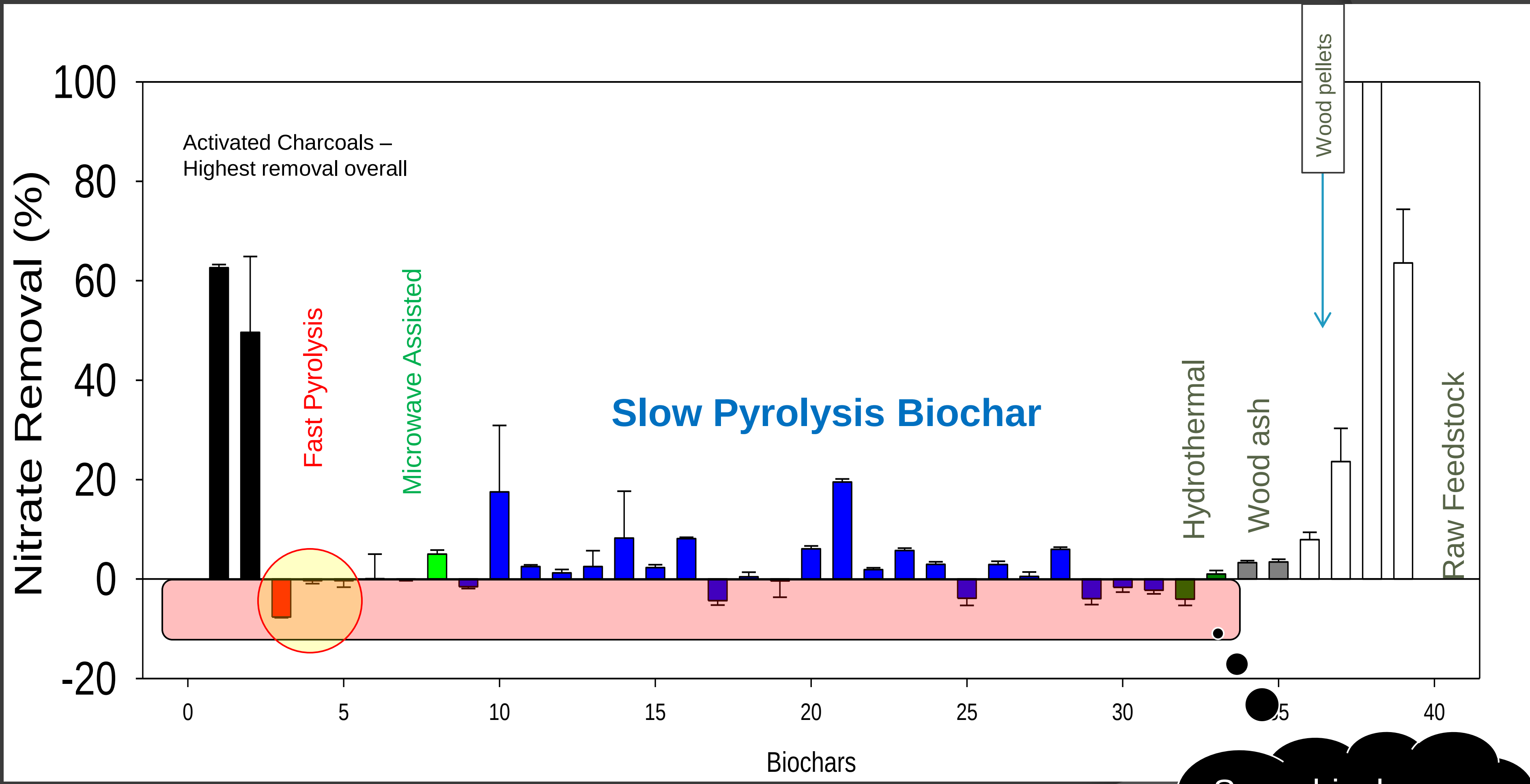
- Activated charcoals best removal of nitrate : 50-63%
- Range of removal efficiencies for biochar : 5 – 20%
- Significant differences between styles of production

Nitrate removal



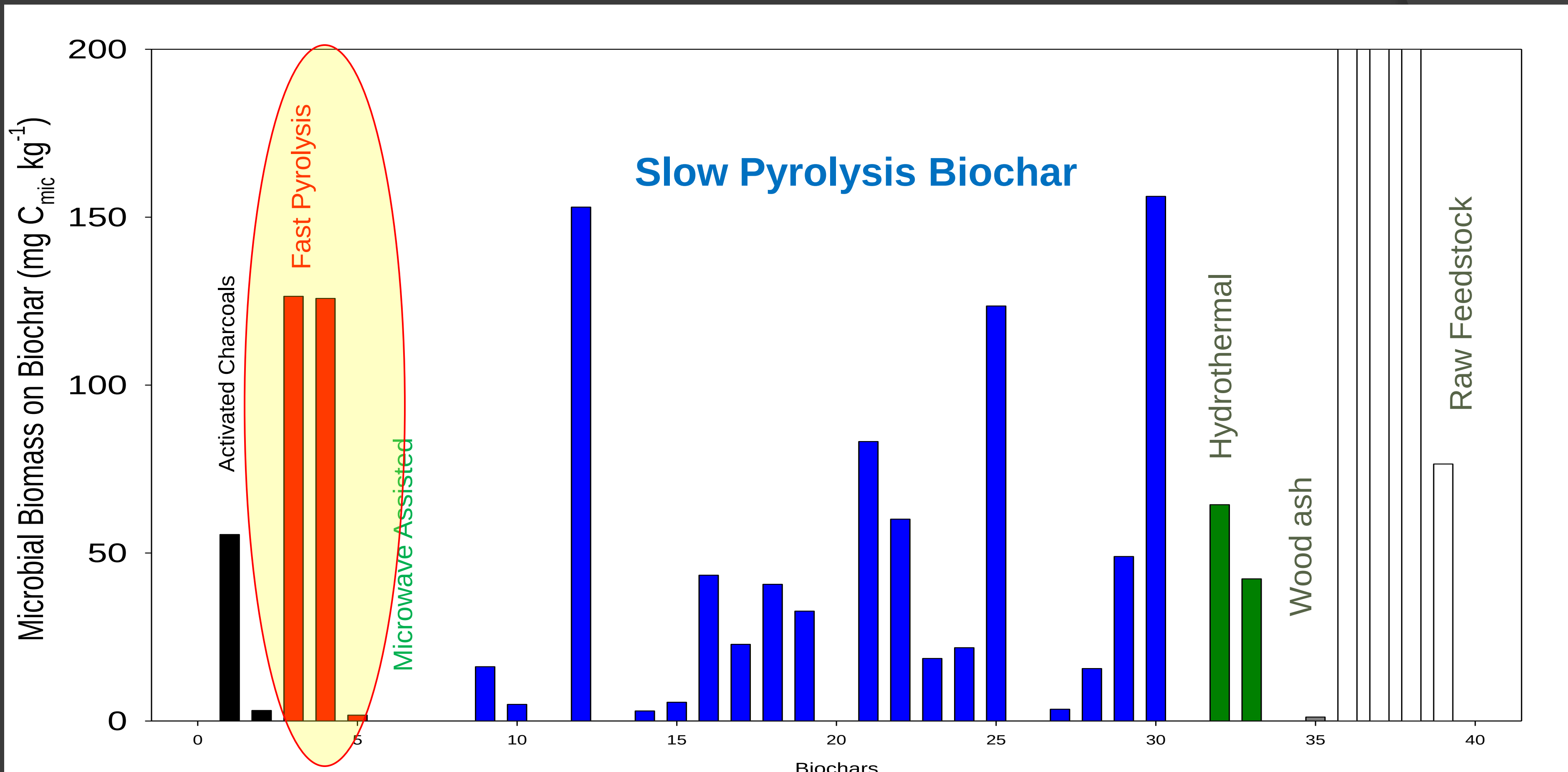
- Switch grass biochar (#21 in graph)
  - Highest removal for slow pyrolysis biochars

Nitrate removal



Some biochars produced nitrate

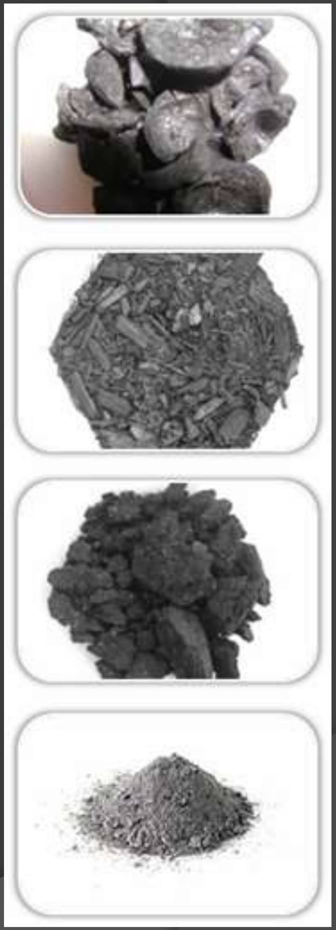
Microbial Content (^{14}C- glucose SIR)



- Range of microbial activity of different biochars

N_2O Biochar Mitigation

- Does sorption of nitrate and ammonium explain the reductions observed in the N_2O production potential for these biochars ?



N_2O Biochar Mitigation

- Does sorption explain the reductions observed in the N_2O production potential for these biochars?

- <u>No</u>
  - Lack of correlation between nitrate sorption and N_2O suppression
  - The fast pyrolysis biochars possess the highest N_2O mitigation potential observed in the lab
    - No observed reduction in nitrate

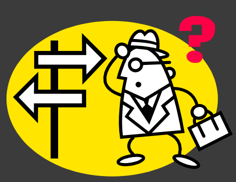
Complications

- Rate of heating can be more important then pyrolysis temperature

  (Kashiwaya and Ishii, 1991; Sahu et al., 1988)
  - These conditions increase number of “active sites”
- pH → ammonia volatilization (Schomberg et al. 2012)
- Microbial presence on biochar
  - Different chars have varying amounts
  - Different species ?
    - Source?
      - Contamination
      - Resistance to pyrolysis – incomplete sterilization? (i.e. fast pyrolysis)

Complications

- Assumed "sorption" could be unanticipated reactions
  - Reaction of charcoal with nitrate causing direct removal of nitrate as N_2 gas



  - Could this be the reason behind the need for fertilize[illegible] with the biochar

Conclusions

- Biochars are complex heterogeneous materials on many levels
  - Surface chemistries
  - Diverse microbial populations on biochar
  - Responses to nitrate/ammonium sorption
- We need to understand biochar's mechanisms
  - Fully utilize the chemical, physical, and microbial properties of biochar to obtain the anticipated function

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