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Towards Reliable Biocarbon Sequestration: Developing Standardized Protocols for Assessing Biochar Stability

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Canada

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- CanmetENERGY-Ottawa's mission is to lead the development of energy S&T solutions for the environmental and economic benefit of Canadians

Outline

- Biochar as a Carbon Sequestration Agent
- Biochar Stability
- Need for Standardized Protocols for Biochar Stability Assessment
- Objectives and Scope of Work
- Review of Biochar Properties Indicative of Biochar Stability
- Candidate Methods for Assessing Biochar Stability
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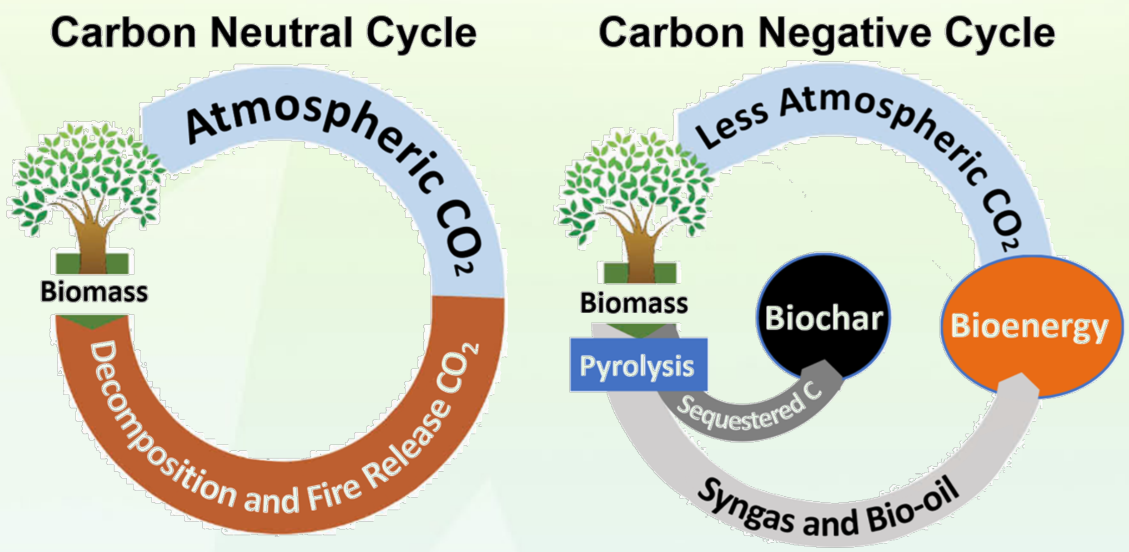
Biochar as Carbon Sequestration Agent

- Biomass residues offer one of the most promising pathways for energy and environmental sustainability.
- Canada alone produces more than 20 million odt/year of roadside residues.
- Unstable biomass residues contribute to significant CO_2 and CH_4 emissions if they are not managed properly.
- Pyrolysis can convert this liability into biochar – a more stable product – that can be stored in soils to sequester carbon.
- Biochar's resistance to decomposition – its stability – serves as a long-term solution for carbon storage.
- The IPCC considers biochar as one of the key carbon dioxide removal (CDR) pathways, required to meet net-zero goals.



Adapted from D. Woolf, J. Lehmann, S. Ogle, A. W. Kishimoto-Mo, B. McConkey, and J. Baldock, "Greenhouse Gas Inventory Model for Biochar Additions to Soil," Environ. Sci. Technol., vol. 55, no. 21, pp. 14795–14805, Nov. 2021, doi: 10.1021/acs.est.1c02425.

Biochar Stability

- Biochar stability in the soil may vary from decades to millennia.
- Permanence of biochar is a necessary condition for creditable CO_2 emissions offsets. Typically, 100-year permanence period is considered acceptable for creditable CO_2 emissions offsets.
- However, it is difficult to measure actual biochar persistence in soils because of long incubation times.
- Multiple approaches have been proposed to simulate and indirectly determine carbon persistence in the soil.
- These methods include chemical, thermal and structural characterization techniques.

Need For Standardized Protocols

- Robust protocols are imperative to verify and ascertain biochar's effectiveness in offsetting carbon emissions.
- Currently, there is a lack of precision, consistency and consensus on accepted methods to characterize biochar stability.
- Published studies on individual methods demonstrate:
  - Different methods of preparing samples (i.e. washing, particle size, etc.)
  - Different temperatures and residence time for the same methods
- This creates confusion, uncertainty, prevents comparison between reported results and reduces confidence in predicted stability.

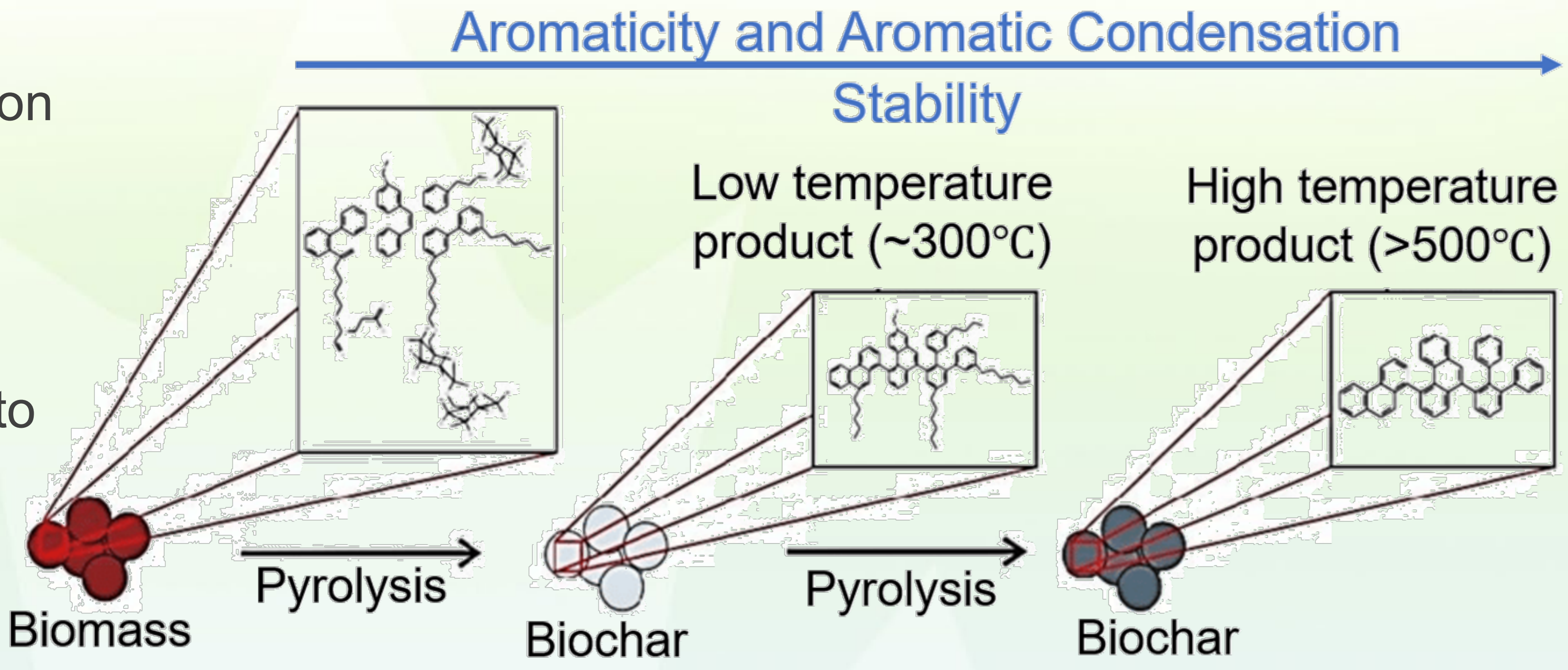
Objectives and Scope of Work

Develop consistent and precise protocols for the assessment of biochar stability.

- Review of the technical literature for key properties of biochar that are indicative of stability.
- Review of the technical literature for prominent methods accessible in terms of low cost and low complexity that are applied for the assessment of biochar stability as candidates for further development.
- Carry out method development that resolves issues around inconsistencies, clarity and precision among candidate methods through harmonization, consolidation and statistical analysis.

Indicators of Biochar Stability: Carbon Structure

- **Aromaticity**: proportion of carbon that is contained within a delocalized pi-electron system
- **Degree of aromatic condensation**: the extent to which aromatic rings are fused to form an extensive aromatic system
- **Elemental composition:** proportions of elements. For instance, proportions of H and O decrease while that of C increases with increased stability



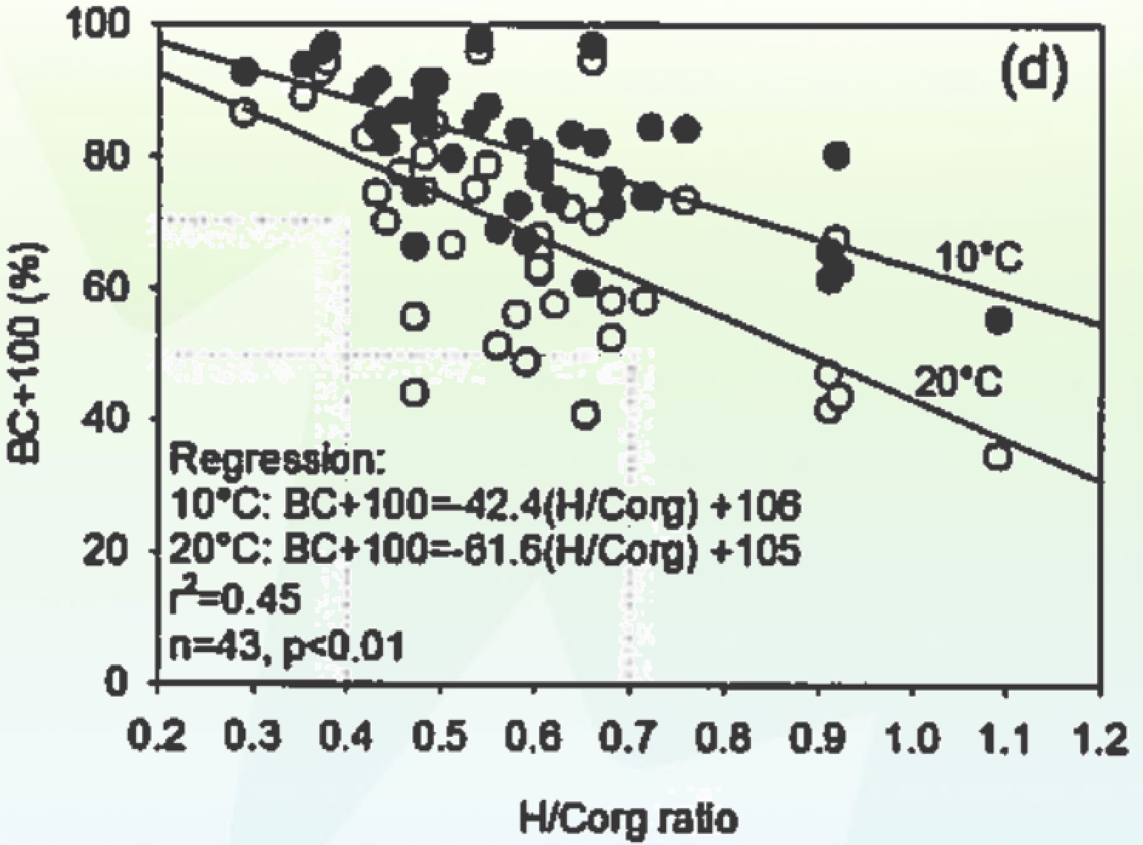
Adapted from G. Cimò, "Characterization of Chemical and Physical Properties of Biochar for Energy Purposes and Environmental Restoration," 2014.

Indicators of Biochar Stability: Chemical Composition

- Carbon in biochar is heterogeneous and can be subdivided into stable, labile and inorganic fractions.
- Stable carbon are primarily comprised of aromatic rings and condensed aromatic sheets.
- Labile fractions consist of incompletely pyrolyzed biopolymers such as glycolipids, phospholipids, and carbohydrates, which decompose much more quickly in the environment.
- Inorganic carbon is found as carbonates that associate with mineral and metal cations in the ash.

Candidate Methods for Assessing Biochar Stability: Elemental Ratios

- Elemental ratios measure against carbon structure and are readily available from universally applied elemental analysis
- $H:C_{org}$ and $O:C_{org}$ are common ratios that that infer biochar stability
- The International Biochar Initiative (IBI) recommends $H:C_{org}$ to compare relative stabilities.
- $O:C_{org}$ is primarily influenced by aromaticity; whereas $H:C_{org}$ is influenced by both aromaticity and degree of condensation.
- Greater correlation exists for $H:C_{org}$ and mean residence time (MRT) in soils and BC_{+100} (biochar carbon remaining in soils after 100 years).



J. Lehmann et al., "Persistence of biochar in soil," in Biochar for Environmental Management: Science, Technology and Implementation, 2nd ed., Taylor & Francis Group, 2015, pp. 235–282

Candidate Methods for Assessing Biochar Stability: Elemental Ratios

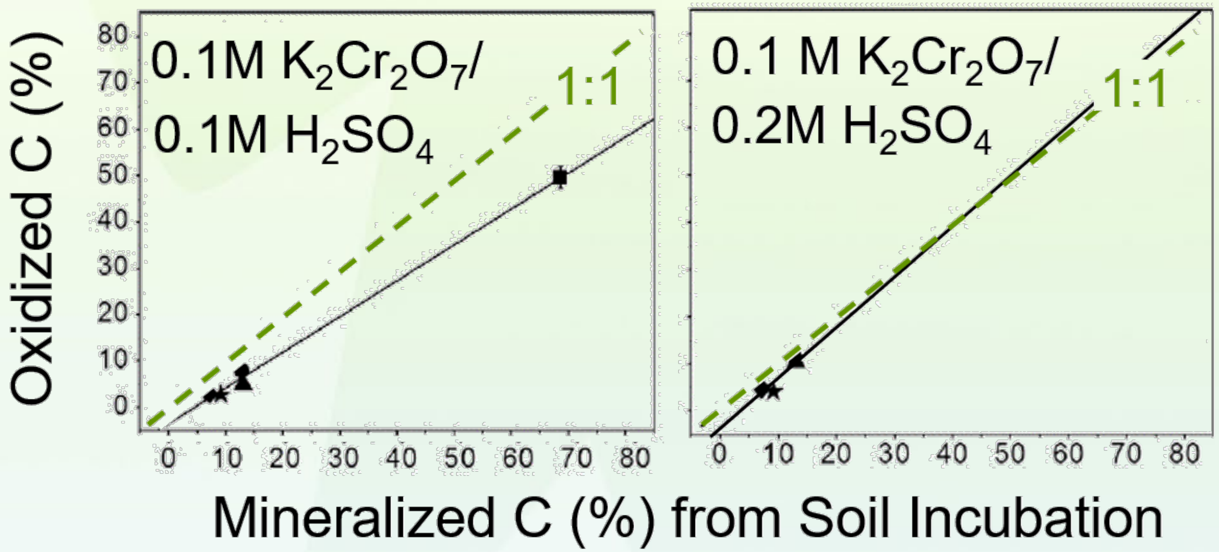
- Indices have been formulated measuring against carbon structure and predict aromaticity based on elemental ratios of C, H and O, but also N and S.

$$AI_{mod} = \frac{1 + C - 0.5\,O - S - 0.5(H + N)}{C - 0.5\,O - N - S}$$

- The modified aromaticity index (AI_{mod}) is a modification to its predecessor AI.
- These indices assume different proportions of O that are carbonyl vs. double bonded.
- AI assumes 100% carbonyl oxygen and has been successfully predicted development of aromaticity within natural organic matter (NOM) in soils.
- AI_{mod} assumes 50%, which resembles more the carbonyl character expected in biochar vs. NOM

Candidate Methods for Assessing Biochar Stability: Chemically Accelerated Aging

- A chemical treatment is used to simulate mineralization in soils by causing selective loss of labile fractions of C
- Application of widely used oxidizing chemicals – H_2O_2, $K_2Cr_2O_7$, and $KMnO_4$.
- A treatment of 0.1M $K_2Cr_2O_7$ in 0.2M H_2SO_4, heated at 100℃ for 2 hours, closely aligns with biochar incubation data extrapolated for a 100-year period in soils.



B. Liu et al., "A fast chemical oxidation method for predicting the long-term mineralization of biochar in soils," Science of The Total Environment, vol. 718, p. 137390, May 2020, doi: 10.1016/j.scitotenv.2020.137390.

Candidate Methods for Assessing Biochar Stability: Resistance to Thermal Degradation

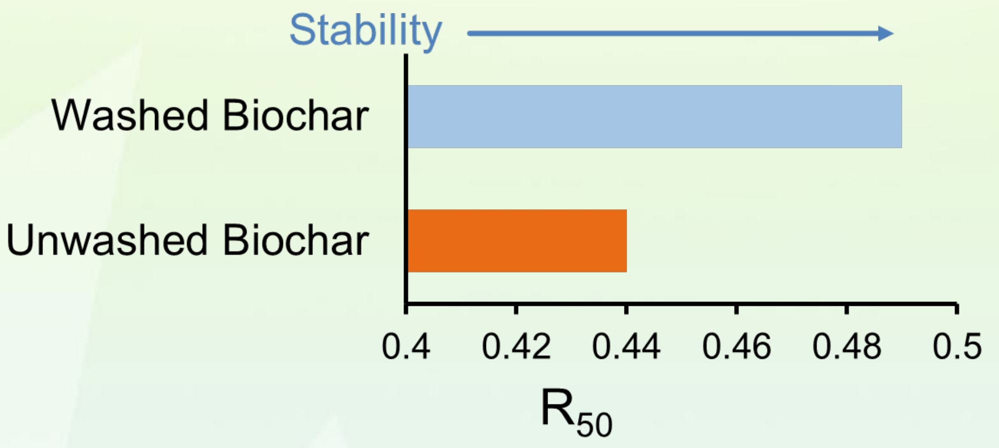
- Biochar stability may be inferred from resistance to thermal stress.
- Recalcitrance index (R_{50}) is used as a metric for biochar stability.
- Higher values suggest higher degradation resistance and greater stability.

$$R_{50} = \frac{T_{50,x}}{T_{50,graphite}}$$

- $T_{50,x}$ is the temperature when 50% of the biochar sample is oxidized.
- $T_{50,graphite}$ is the reference temperature when 50% of graphite is oxidized (886℃)

Method Standardization Efforts

- Much like how biochar treatment conditions may be calibrated, the form and nature of biochar samples prior to treatment may impact measured stability.
- Evidence shows impacts of biochar particle size on mineralization kinetics.
- Moreover, washing of biochar samples with distilled water – thought to mimic natural water runoff and removes biochar inorganics – alters perceived stability.
- Candidate methods will be tested with uniformly-prepared biochar to enable fair comparison.
- Statistics will be compiled on impacts of increased prescription to methods (i.e. particle-size, washing vs. no washing, etc.) to enable formulation of precise and repeatable methods.



N. Gómez, J. G. Rosas, S. Singh, A. B. Ross, M. E. Sánchez, and J. Cara, “Development of a gained stability index for describing biochar stability: Relation of high recalcitrance index (R50) with accelerated ageing tests,” Journal of Analytical and Applied Pyrolysis, vol. 120, pp. 37–44, Jul. 2016, doi: 10.1016/j.jaap.2016.04.007

Closing Remarks

- Numerous methods exist in the literature to measure biochar stability.
- It is difficult to compare and correlate measurements to actual persistence in soil (i.e. MRT, BC_{+100}, etc.).
- Prominent techniques that are used to evaluate biochar stability require additional prescription and harmonization to allow fair and reliable comparison.
- Areas of inconsistencies and lack of clarity across multiple methods will be resolved through statistical analysis of impacts from increased prescription and consolidation.
- Future work will require confidence in results through substantiation of repeatability, accuracy and precision (i.e. round-robin studies).

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Thank you!

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