NextChar @Biochar 2019

Options for Characterizing Biochar and Evaluating Quality

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July 2, 2019

First, some necessary mechanics of getting subtle and quantitative concepts across via PowerPoint with verbal embellishment and sharing the audience's bandwidth with every distraction money can buy .....

While 15 minutes of Fame will fit in a 17 minute time slot, this talk, consisting of 53 slides, will not.

Therefore, the slides are partially self-explanatory and the conclusions are called out clearly. The portion of the talk we don't get to can be viewed on the **pdf if and when it is posted by the conference or posted elsewhere**. I will shortly make the pdf available at web sites I control or have access to.

Summary of the Conclusions

- Drying biochar is a compromise – it impacts all subsequent measurements and can ruin them if done improperly. Any drying of biochar removes VOCs and moisture together.
- Both IBI and EBC methods for Volatile Matter decompose ash carbonates and count them as VM; EBC counts them in ash also.
- C_{org} is calculated by C_{total}-C_{inorg}, where the C_{inorg} test is not quantitative. Unreacted carbonates are added to C_{org} .
- H includes any residual moisture, including inorganic hydrates, increasing H measurement from the CHNO analysis
- H/C_{org} accumulates all the errors of the prior tests.
- **Virtually all reported biochar characterization data suffer from excessive systematic errors due to the IBI/EBC protocols. *Most errors are easily avoided with proper analytical methods.***

NextChar @Biochar 2018

Biochar Standards and Characterization Schemes:

How and What is being measured, and What is it actually telling you

Basically a comparison of:

- ***IBI Biochar Standards V2.1***
- ***EBC: European Biochar Certificate***
- ***BBM: Baseline Biochar Metrics***

The Baseline Biochar Metrics grew out of an effort in 2016 that included a presentation at USBI2016, archived as paper 3.4.3 MCLAUGHLIN, Hugh.pdf at http://biochar-us.org/2016-biochar-symposium

Presentation at USBI2016, Corvallis, OR

NextChar Characterization Matrix

Measuring biochar properties to establish Valuation

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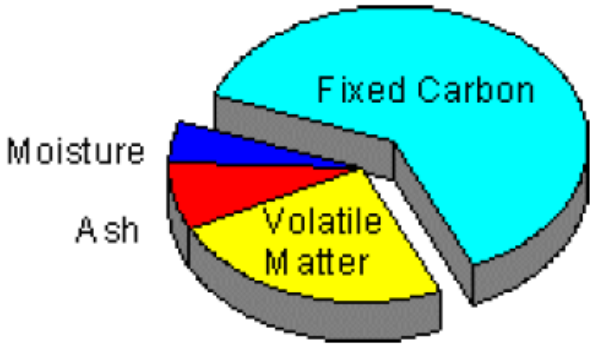
August, 2016

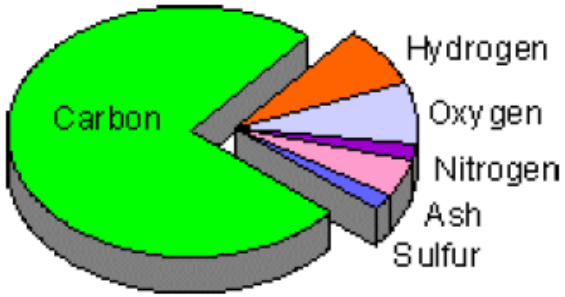
FIGURE 4: PROXIMATE AND ULTIMATE ANALYSES OF COALS

Proximate Analysis

Determines (on an as-received basis)

- **Moisture content**
- **Volatile matter** (gases released when coal is heated).
- **Fixed carbon** (solid fuel left after the volatile matter is driven off, but not just carbon).
- **Ash** (impurities consisting of silica, iron, alumina, and other incombustible matter).





Source: U.S. DOE - EIA, Coal Data: A Reference, 1989.

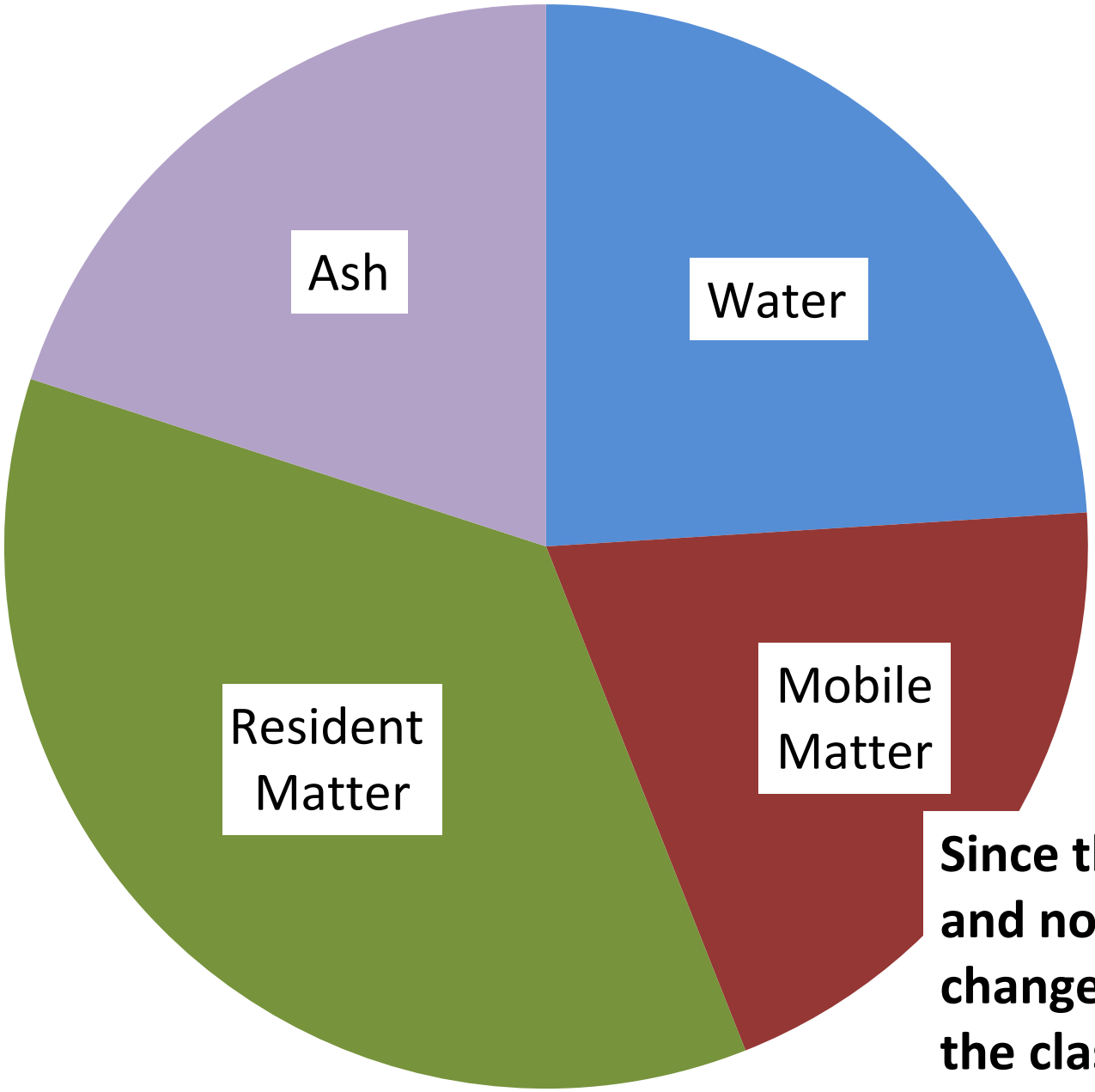
Ultimate Analysis

Determines the amount of carbon, hydrogen, oxygen, nitrogen, and sulfur.

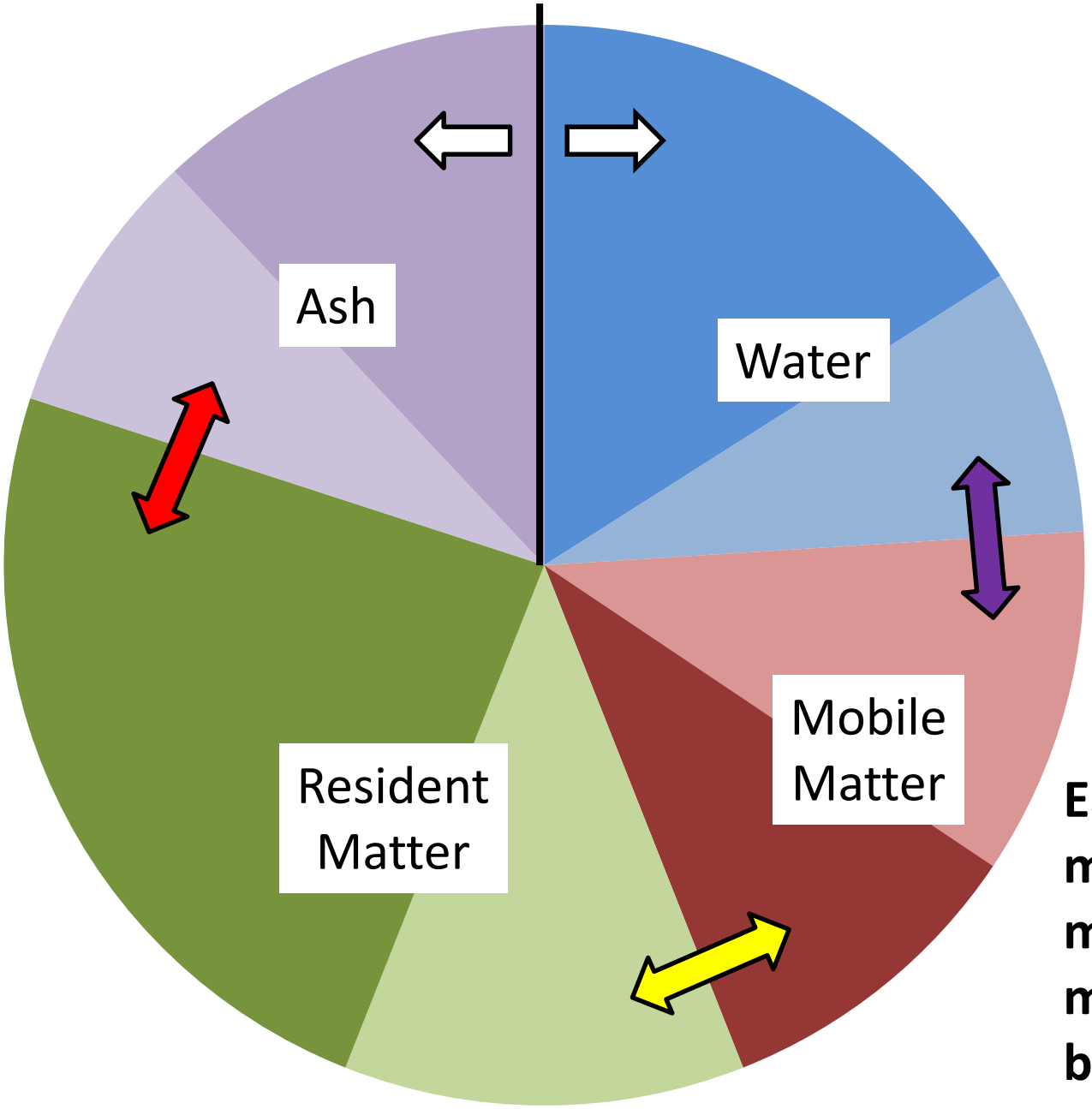
- **Btu -** Heating value is determined in terms of Btu both on an as-received basis (including moisture) and on a dry basis.
- The carbon is from both the volatile and fixed matter, not differentiated.

From All Biochars Paper, V2, Oct 2009

From: http://www.coaleducation.org/ky_coal_facts/coal_resources/coal_properties.htm



Since this is Biochar, and not Coal, we will change the titles of the classes of materials



- free water
- bound water
- VOCs
- SVOCs
- NVOCs
- Turbostratic
- Ash Volatiles
- Ash Non-volatiles

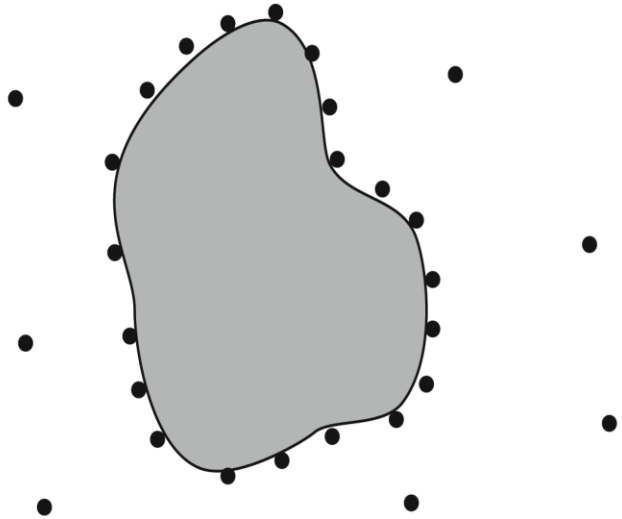
Each group is actuall made up or two, or more , types of materials – which behave differently…

First, let's dry the biochar

Moisture levels in biochars range from none (as produced) to 500% of char weight – if flooded and drained. It is often adjusted during handling for dust suppression and responds to ambient conditions – both gives and takes atmospheric moisture.

Many biochars adsorb water vapor at >60%RH, and give it back at <40%RH, and the amount of involved is significant (>10wt%)

The conditions that remove water, especially adsorbed water, also remove Volatile Organic Compounds (VOCs), which we aspire to measure as part of the Mobile Matter weight fraction ……



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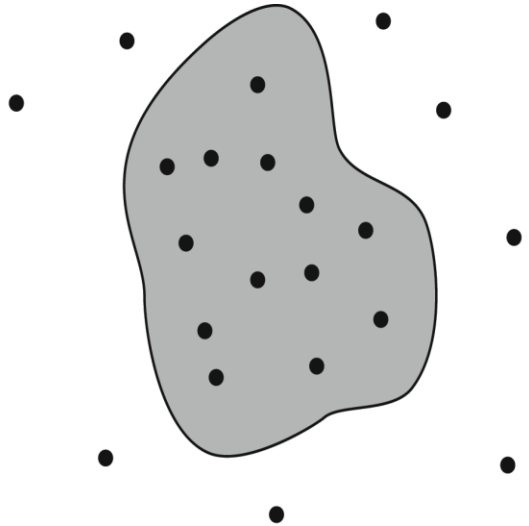

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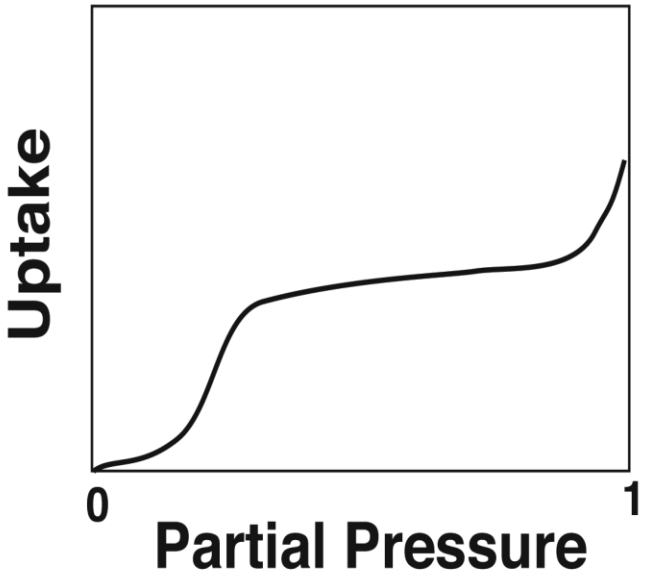
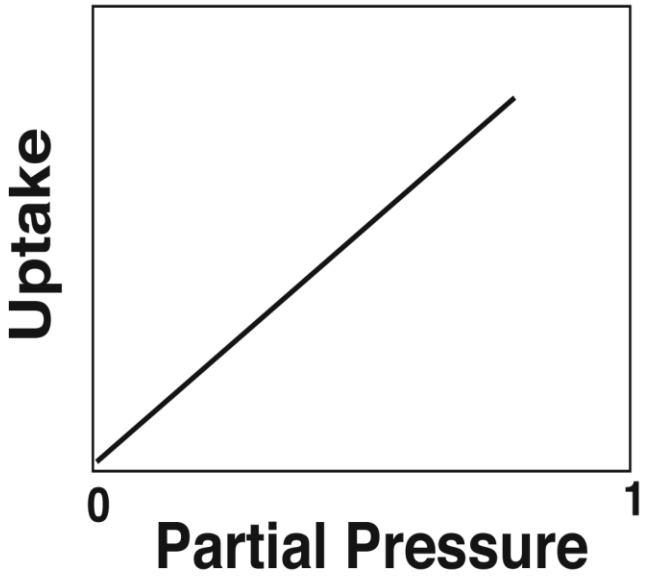
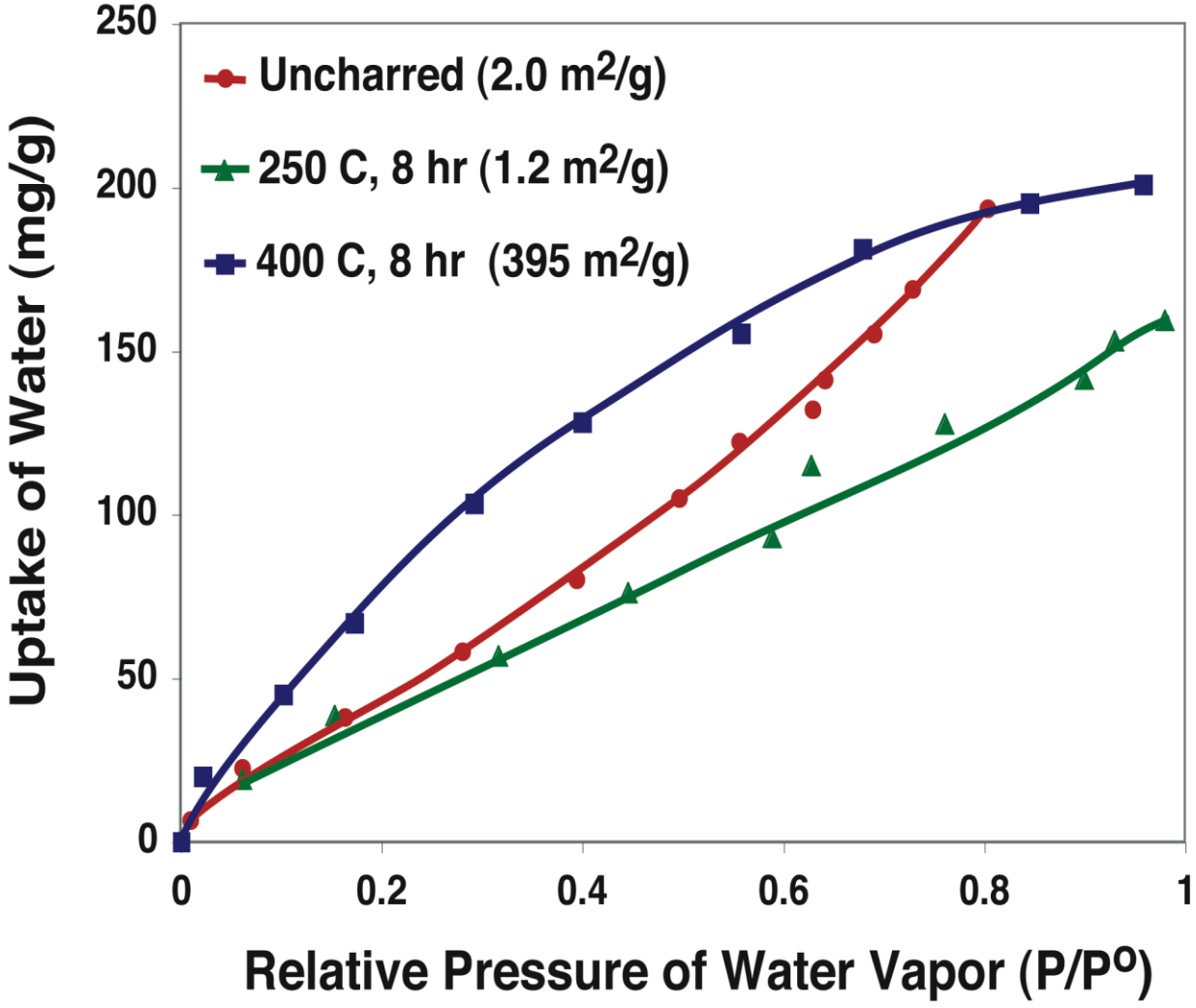


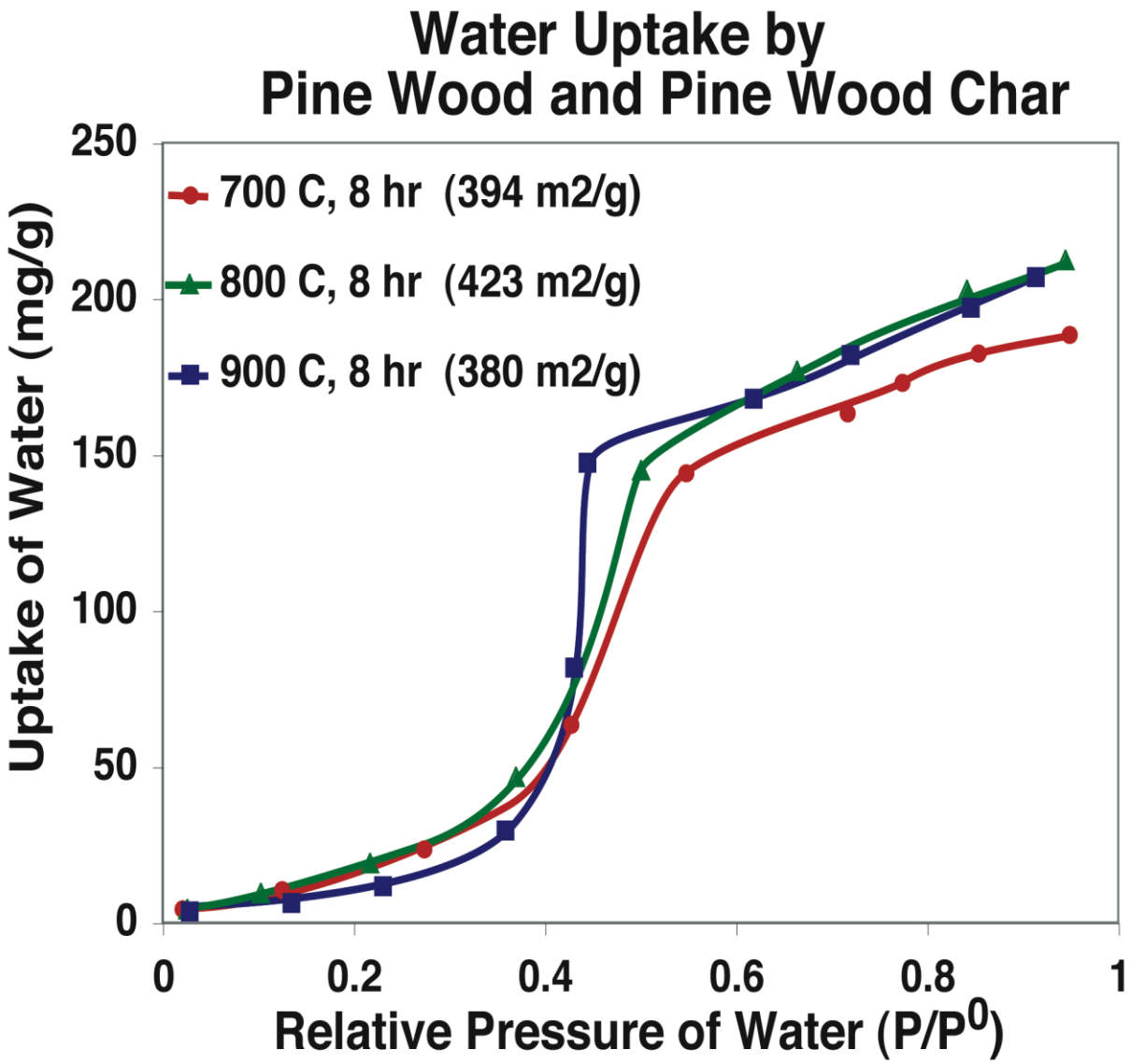


USGS
science for a changing world

Water Uptake by Pine Wood and Pine Wood Char



USGS
science for a changing world



USGS
science for a changing world

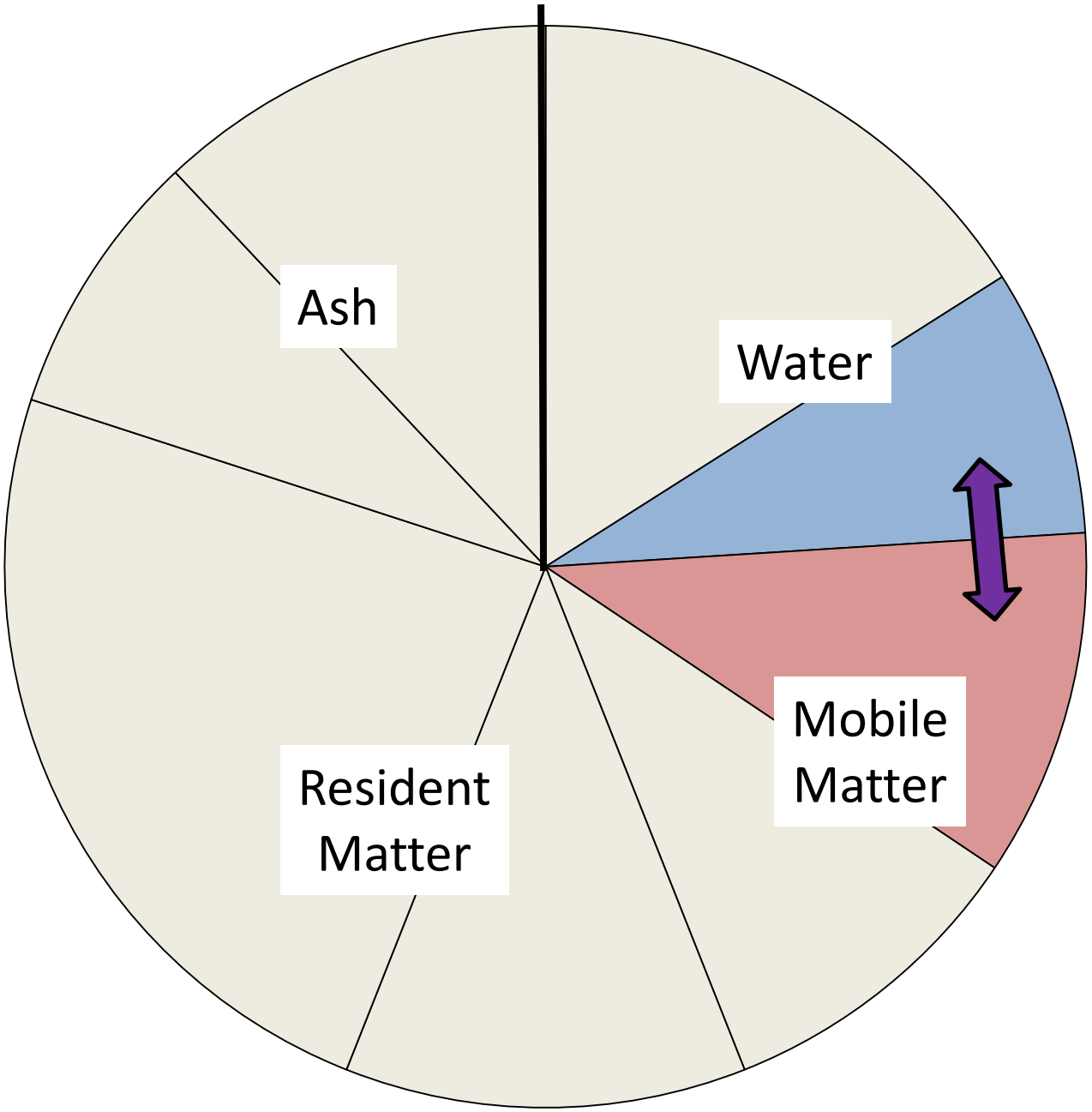
EBC vs IBI vs BBM Sanity check

European Biochar Certificate V4.8 – Required (Water content) - DIN 51718 method A Two step: raw moisture at (40 ± 2)°C until constant mass; hygroscopic moisture in TGA crucible and nitrogen atmosphere **at (106 ± 2) ° C** to constant mass.

IBI Test Method – Required (Moisture content) ASTM D1762-84 'Standard Test Method for Chemical Analysis of Wood Charcoal' **Moisture content at 105 °C for 2 hours**. Note 2: The sample shall be considered oven-dry when the decrease in weight of consecutive weighings is 0.0005 g or less. **Difficult to achieve for many biochars – even Lehmann, et al. gave up at 18 hours**

BBM Test Method - Required in "Dry Biochar" Procedure
Dry at **145C to 155 ° C** as per ASTM D2867 "Standard Test Methods for Moisture in Activated Carbon" - 3 hrs normally sufficient .


70%
60%
50%
40%
30%
20%
10%
0%
0
2
4
6
8
10
12
14
16
18
20
22
24
I-Cool Terra
II-BLaK I
III-GreenTree
IV-AC1230C
Loss of Moisture - % of starting weight
150C
100C
hours



- free water
- bound water
- VOCs
- SVOCs
- NVOCs
- Turbostratic
- Ash Volatiles
- Ash Non-volatiles

Water and VOCs overlap and desorb together. The mass is going to be assigned to one category; the overlap causes error.

What have we learned:

- Do not go by the expectation in the protocols – they were not written for something as complex as biochars.
- Many methods will work: 18 hrs at 105C, 3 hours at 150C, 1 to 2 hour at 200C (not higher). **Wetted biochars take longer and have greater error due to volatile stripping.** *This cannot be avoided, so live with it.*
- Cover samples to avoid stripping volatiles or don't dry samples in ovens with circulating fans. BBM methods provide simple way to minimize error, but nothing prevents the simultaneous loss of VOCs when removing water vapor – they leave together because that is the Law (of Thermodynamics).

Summary of the Conclusions

- Drying biochar is a compromise – it impacts all subsequent measurements and can ruin them if done improperly. Any drying of biochar removes VOCs and moisture together.
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- H/C_{org} accumulates all the errors of the prior tests.
- **Virtually all reported biochar characterization data suffer from excessive systematic errors due to the IBI/EBC protocols. *Most errors are easily avoided with proper analytical methods.***

Moving onto Ash

If anything is going to be well behaved, it is Ash.

It is conserved under virtually all conditions of the plants life and under the conditions of most pyrolysis – so let's just design a method of seeing how much ash is there and be done with it.

The common consensus is the Ash is not volatile nor reactive, so lets just remove the water and organics and weigh what is left…..

EBC vs IBI vs BBM Sanity check

European Biochar Certificate V4.8 – Required - Declaration
DIN 51719, ISO 1171 or EN 14775 – **ashing at 550°C**
heating at 5 K/min to 106°C under nitrogen atmosphere , weigh, then at 5 K/min to 550 ° C (90 min) under oxygen, hold for 1h

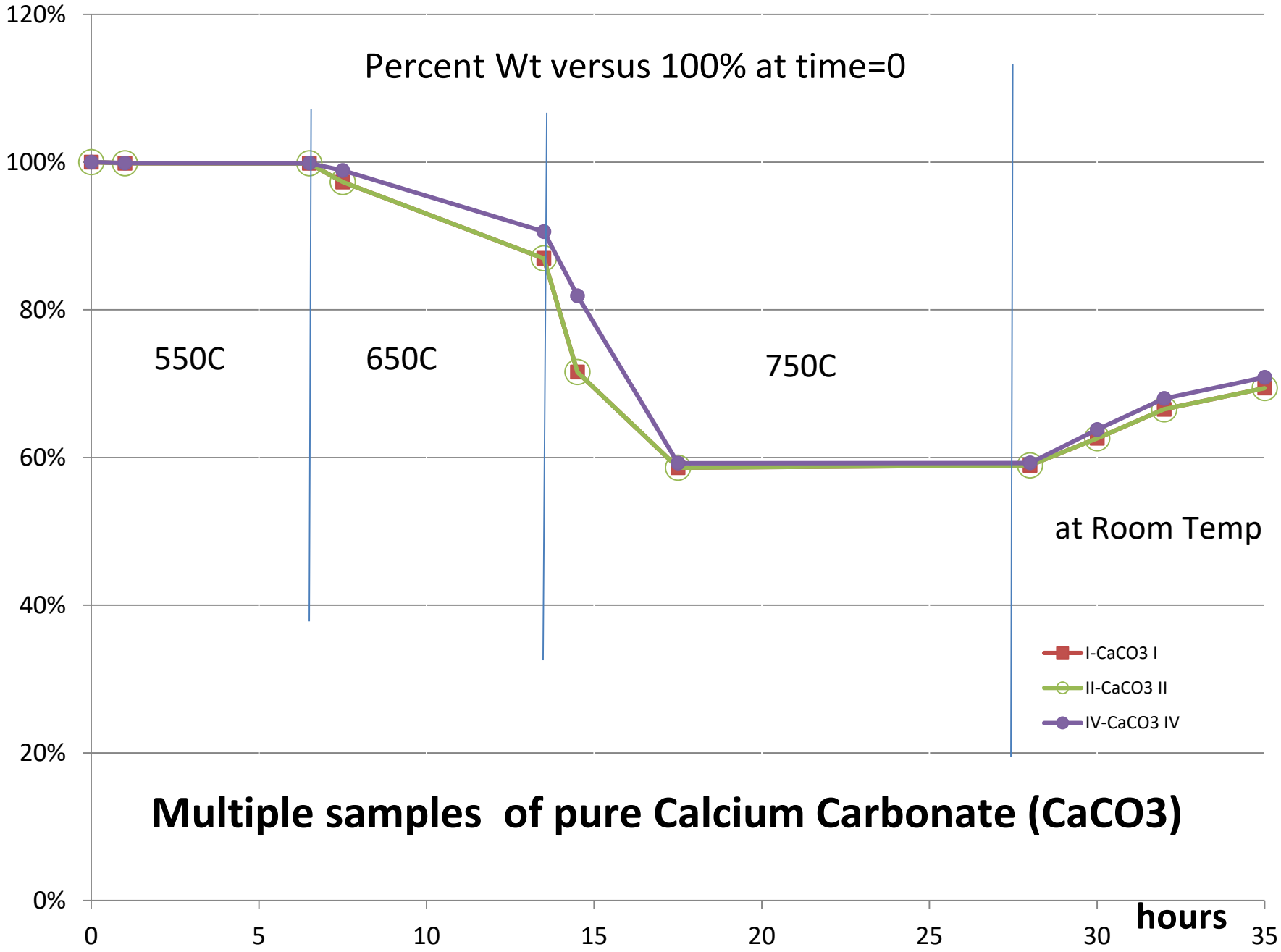
IBI Test Method – Required – Declaration - (% of total mass, dry basis)
ASTM D1762-84 'Standard Test Method for Chemical Analysis of Wood Charcoal'. **Ash at 750 °C for 6 hours.**
Air dried and ground sample, dry at 105C for two hours, **covered volatile matter to 950C**, then ash at 750C for 6 hrs uncovered

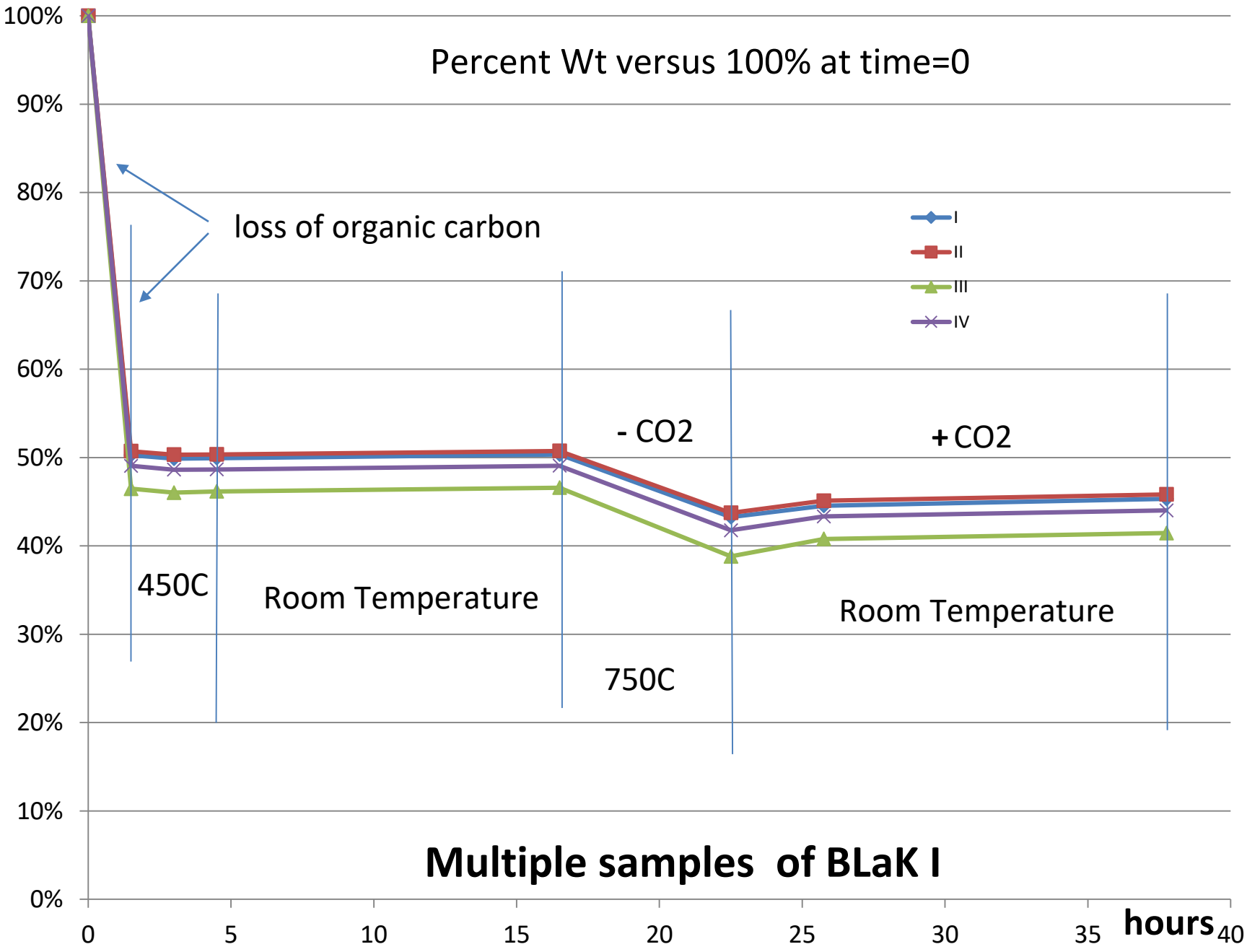
BBM Test Method - Required in "Dry Biochar" Procedure
Dry at 145C to 155C as per ASTM D2867 "Standard Test Methods for Moisture in Activated Carbon" then **Open crucible ashing at 550 ° C in air for two hours** - *similar to EBC Method*

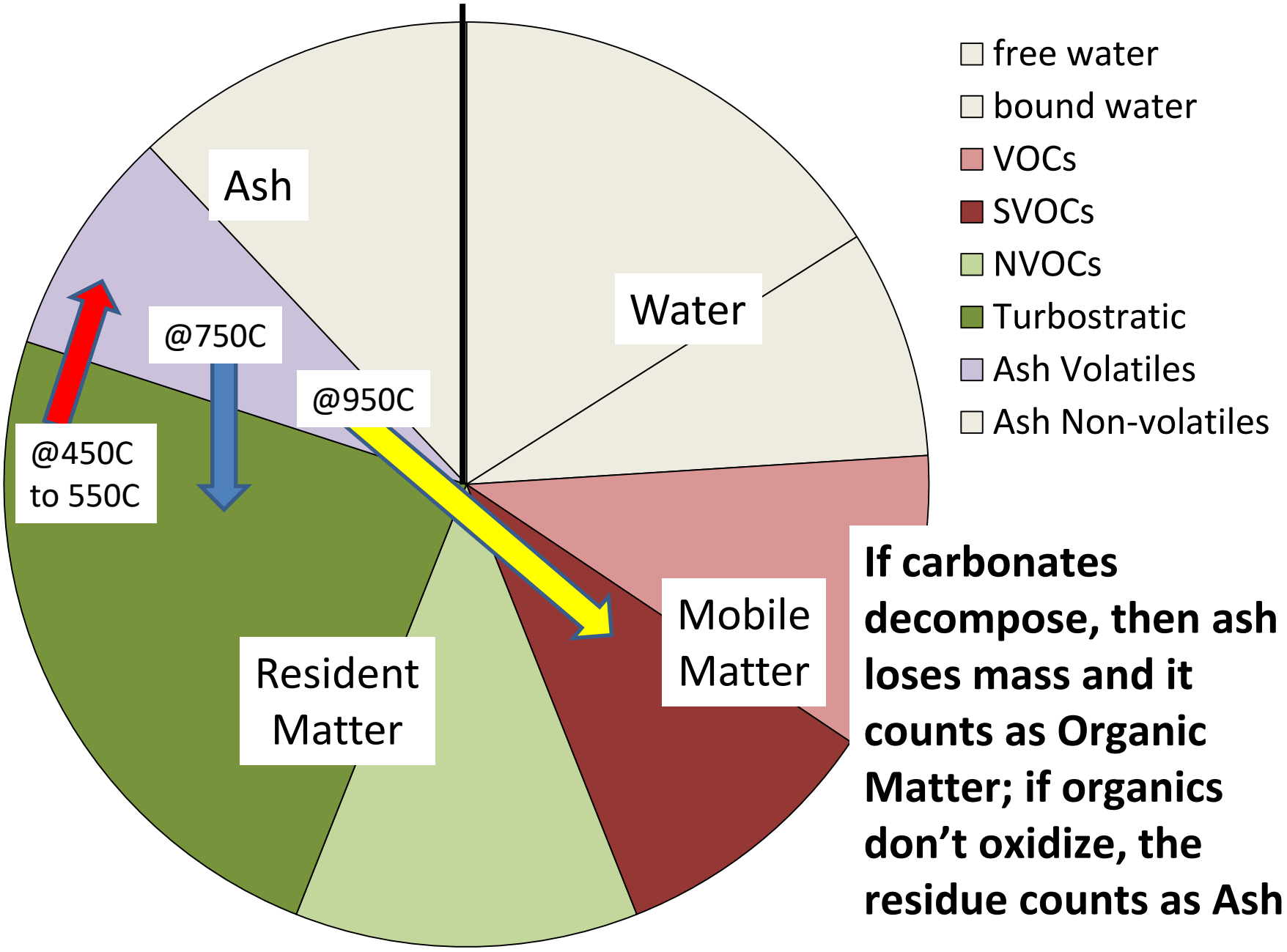
Assumptions need to be confirmed

- "The majority of carbonates in biochar, specifically calcium and potassium carbonates, **resist decomposition at 750 C** (Dean, 1999 = Lange's Handbook), the temperature prescribed by ASTM for quantification of the ash content."

Reference: Bioresource Technology 114 (2012) 644–653, "Characterization of biochars to evaluate recalcitrance and agronomic performance", by Akio Enders, Kelly Hanley, Thea Whitman, **Stephen Joseph, Johannes Lehmann**


Percent Wt versus 100% at time=0
120%
100%
80%
60%
40%
20%
0%
550C
650C
750C
at Room Temp
I-CaCO3 I
II-CaCO3 II
IV-CaCO3 IV
Multiple samples of pure Calcium Carbonate (CaCO3)
0
5
10
15
20
25
30
35
hours


Percent Wt versus 100% at time=0
loss of organic carbon
I
II
III
IV
- CO2
+ CO2
450C
Room Temperature
750C
Room Temperature
Multiple samples of BLaK I
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
5
10
15
20
25
30
35
40
hours



If carbonates decompose, then ash loses mass and it counts as Organic Matter; if organics don't oxidize, the residue counts as Ash

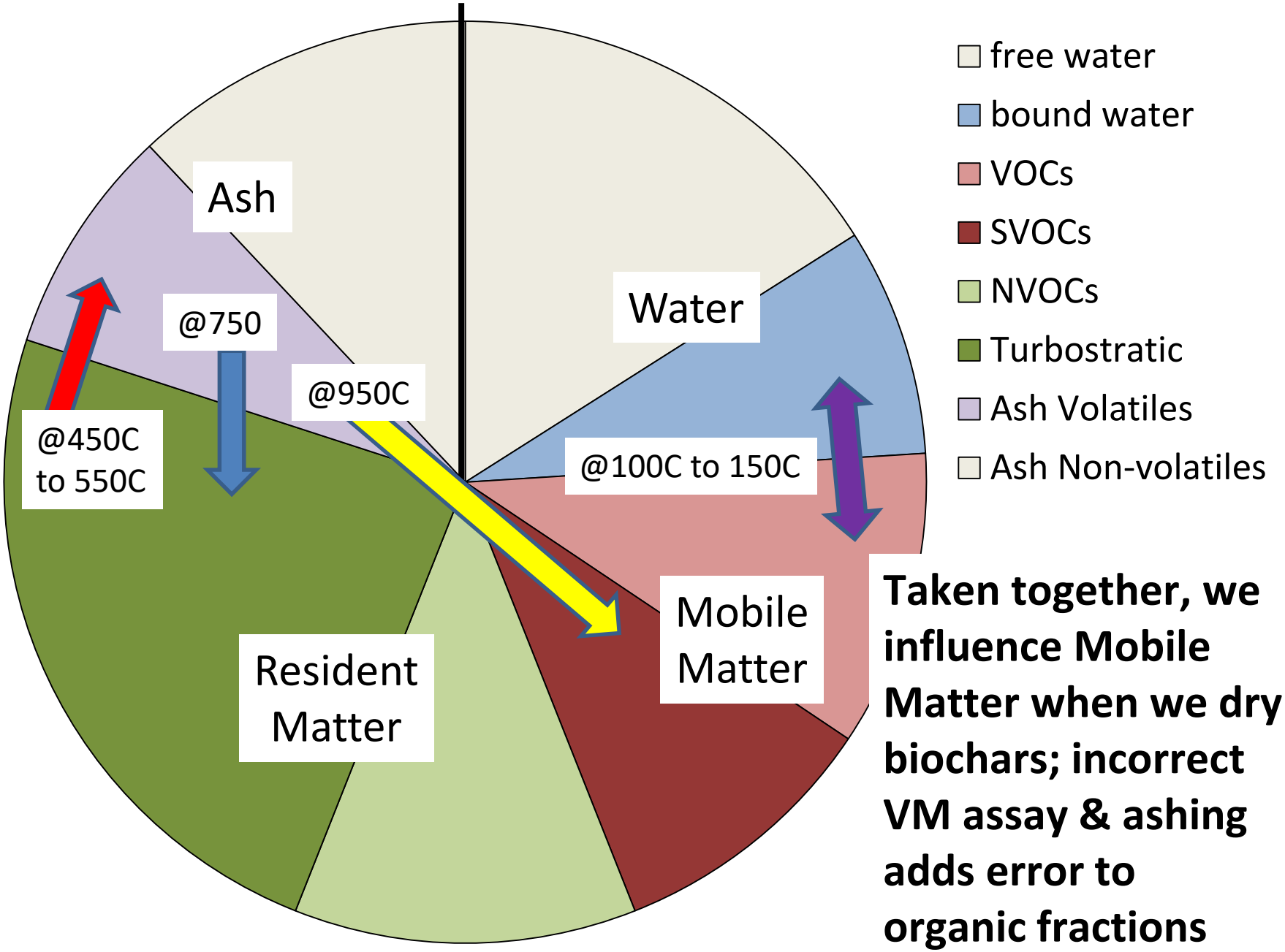
What have we learned:

- **Do not go to 750C** – the carbonates decompose and then reabsorb atmospheric CO2 upon cooling – **an analytical nightmare.**
- BBM procedure uses the tops of the crucibles to present char for ashing in air purged M/F
- Ash until uniform color of residual material
- Grind sample (mortar & pestle) and pass through window screen or finer
- Typical time: 2 hours at 450C to 550C
  - additional holding time does not hurt


2018/06/24 02

Let's summarize the issues so far

- **Drying biochar is a compromise.** Too mild or soon, and moisture is left that counts toward volatile matter or as Hydrogen! Too harsh and volatiles are stripped, being counted as moisture and taking H/Corg = 2+. 150C is recommended due to the need to remove adsorbed moisture in addition to free moisture.
- If ASTM D1762 is used, the VM assay at 950C strips inorganic CO2 from carbonates, which are counted as Volatile Matter (VM is removed before ashing in D1762).
- If Ash is measured at 750C without removing the VM, then the carbonates get counted as Organic Matter.
- **At 450C to 550C, biochars will ash slowly and retain carbonates in the remaining ash portion.** This method is safe, easily monitored and uses less expensive furnaces.



Taken together, we influence Mobile Matter when we dry biochars; incorrect VM assay & ashing adds error to organic fractions

Summary of the Conclusions

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Finally, let's do MM vs RM, and H/Corg

Mobile Matter ⇔ VOCs & SVOCs ⇔ Labile Matter is a class of materials characterized by what it is not – stable carbon that will not break down in the soil. It is related to, but not the same as, the vapors that are created and released by the coexisting solid phase throughout the pyrolysis process. Mobile matter converts into vapors and additional Resident Matter.

Any time a char experiences a higher temperature for the first time, it undergoes "incremental carbonization", where the solid phase further consolidates into more stable forms and a portion of the original solid is converted to volatiles, which are released as vapor and reduce the weight of the remaining solid. **As such, ASTM D1762: Volatile Matter measures the total weight of vapors created after the starting char is converted to 100% Fixed Carbon at 950C.**

Note: Nobody knows what is going on here, since pore space is turning into char …

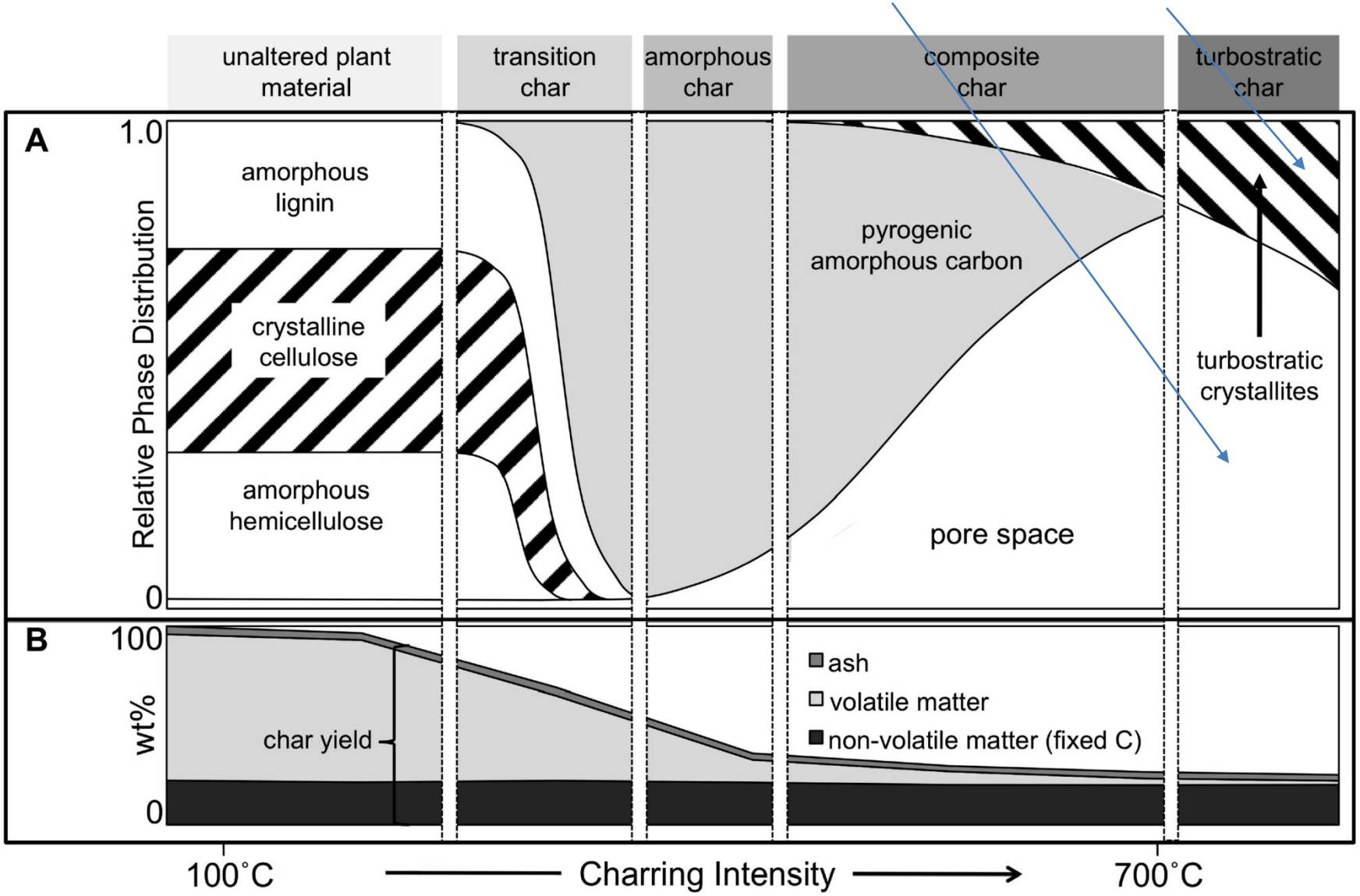


Figure 4 from *Environ. Sci. Technol.* ***2010, 44, 1247–1253***

IBI Biochar Standard "Metrics"

Table 1. Test Category A Parameters, Criteria, and Test Methods.

Test Category A: Basic Utility Properties (Required for All Biochars)			
Parameter	**Criteria[1]**	**Unit**	**Test Method[2]**
Moisture	Declaration	% of total mass, dry basis	ASTM D1762-84 Standard Test Method for Chemical Analysis of Wood Charcoal (specify measurement date with respect to time from production)
Organic Carbon (C_{org})	10% Minimum *Class 1*: ≥60% *Class 2*: ≥30% and <60% *Class 3*: ≥10% and <30%	% of total mass, dry basis	Total C and H analysis by dry combustion-elemental analyzer. Inorganic C analysis by determination of CO_2-C content with 1N HCl, as outlined in ASTM D4373 Standard Test Method for Rapid Determination of Carbonate Content of Soils. Organic C calculated as Total C – Inorganic C. See Appendix 7 for $H:C_{org}$ discussion.
$H:C_{org}$	0.7 Maximum	Molar ratio	
Total Ash	Declaration	% of total mass, dry basis	ASTM D1762-84 Standard Test Method for Chemical Analysis of Wood Charcoal
Volatile Matter	Declaration	% of total mass, dry basis	ASTM D1762-84 Standard Test Method for Chemical Analysis of Wood Charcoal

Designation: D1762 – 84 (Reapproved 2013)

Standard Test Method for Chemical Analysis of Wood Charcoal[1]

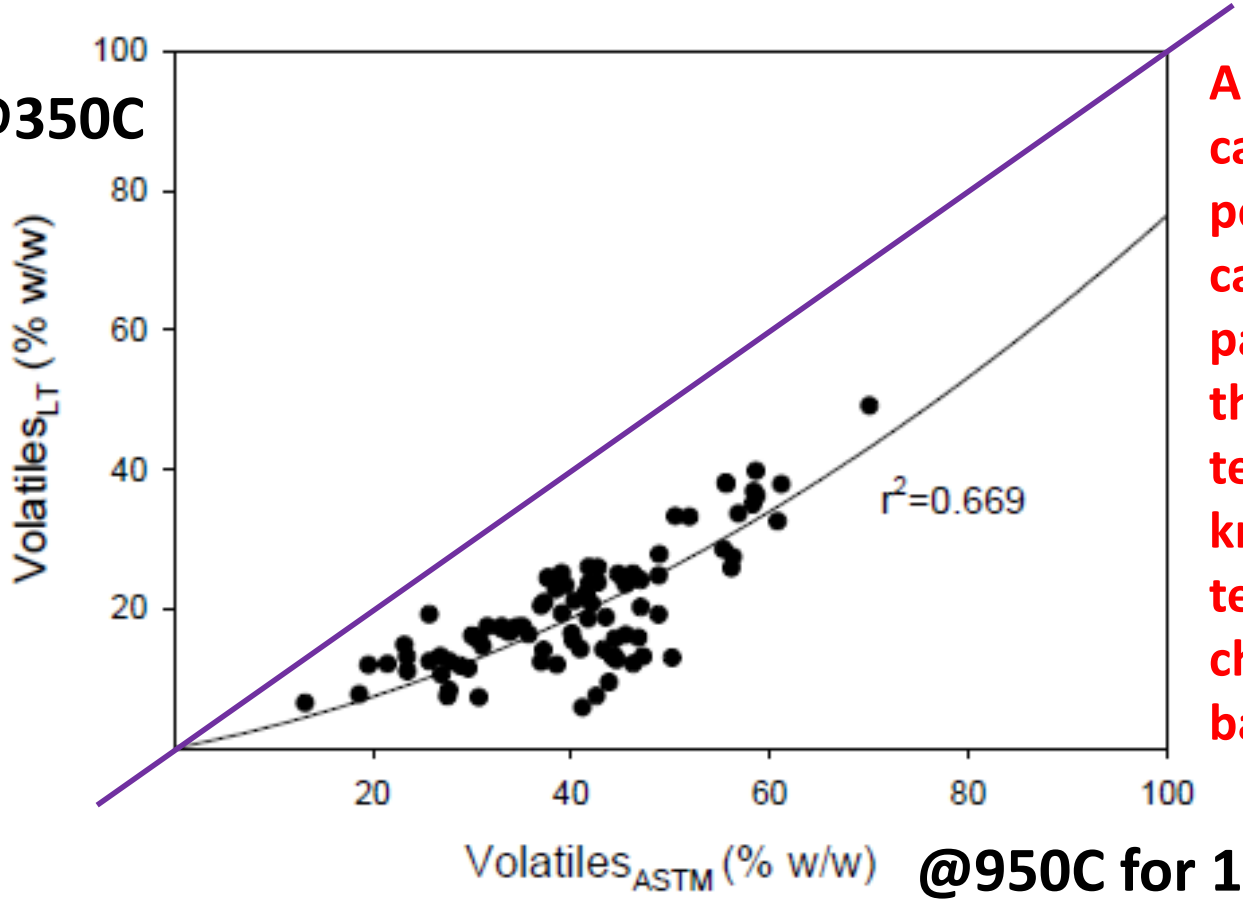
Audience: Has anyone ever seen a Proximate Analysis with duplicate results reported?

7.1 Make duplicate determinations.

7.3 *Volatile Matter*—Heat the muffle furnace to 950°C. Preheat the crucibles used for the moisture determination, with lids in place and containing the sample, as follows: with the furnace door open, for 2 min on the outer ledge of the furnace (300°C) and then for 3 min on the edge of the furnace (500°C) (Note 3). Then move the samples to the rear of the furnace for 6 min with the muffle door closed. Watch the samples through a small peep-hole in the muffle door. If sparking occurs, results will be in error (Note 4). Cool the samples in a desiccator for 1 h and weigh.


This is a Muffle Furnace at 950C when you open the door
2019/03/24 04:26 PM

@350C



Alternate temperatures can used to drive off a portion of the organic carbon. BBM uses 450C to parse Mobile Matter from the Resident Matter. Any temperature works, but knowing what the split is telling you is the challenge and must be based on science ……

@950C for 10 minutes, no stages

Supplementary Fig. S1. Relationship between volatile contents determined by ASTM and the modified LT method (see text for description of methods; n=2).

Bioresource Technology 114 (2012) 644–653, Supplementary Online Material, pg 38 of 43

Some have tried to make a silk purse out of a sow's ear:

Journal of Analytical and Applied Pyrolysis 124 (2017) 335–342

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Modified method for proximate analysis of biochars

Deborah Aller, Santanu Bakshi, David A. Laird*

Department of Agronomy, Iowa State University, Ames, IA 50011, USA

A B S T R A C T

Proximate analysis is widely used to determine moisture, volatile matter (VM), fixed carbon (FC) and ash content of biochars. The original ASTM D1762-84 method was developed to assess quality of hardwood charcoal for use as fuel. We have developed a modified proximate analysis method to assess quality of diverse biochars for use as soil amendments. We determined that a N_2 purge is necessary during both moisture and VM determination to avoid errors associated with sample oxidation. We assessed a range of boundary temperatures (350–950 °C) for separating VM and FC, and determined that 800 °C is the minimum temperature required to distinguish between VM and FC in biochars. Furthermore, correlation between VM/FC and molar H/C_{org} ratios suggests that VM/FC ratios are a useful measure of biochar stability. Use of the proposed modified method is encouraged to reduce variance in analytical results among studies.

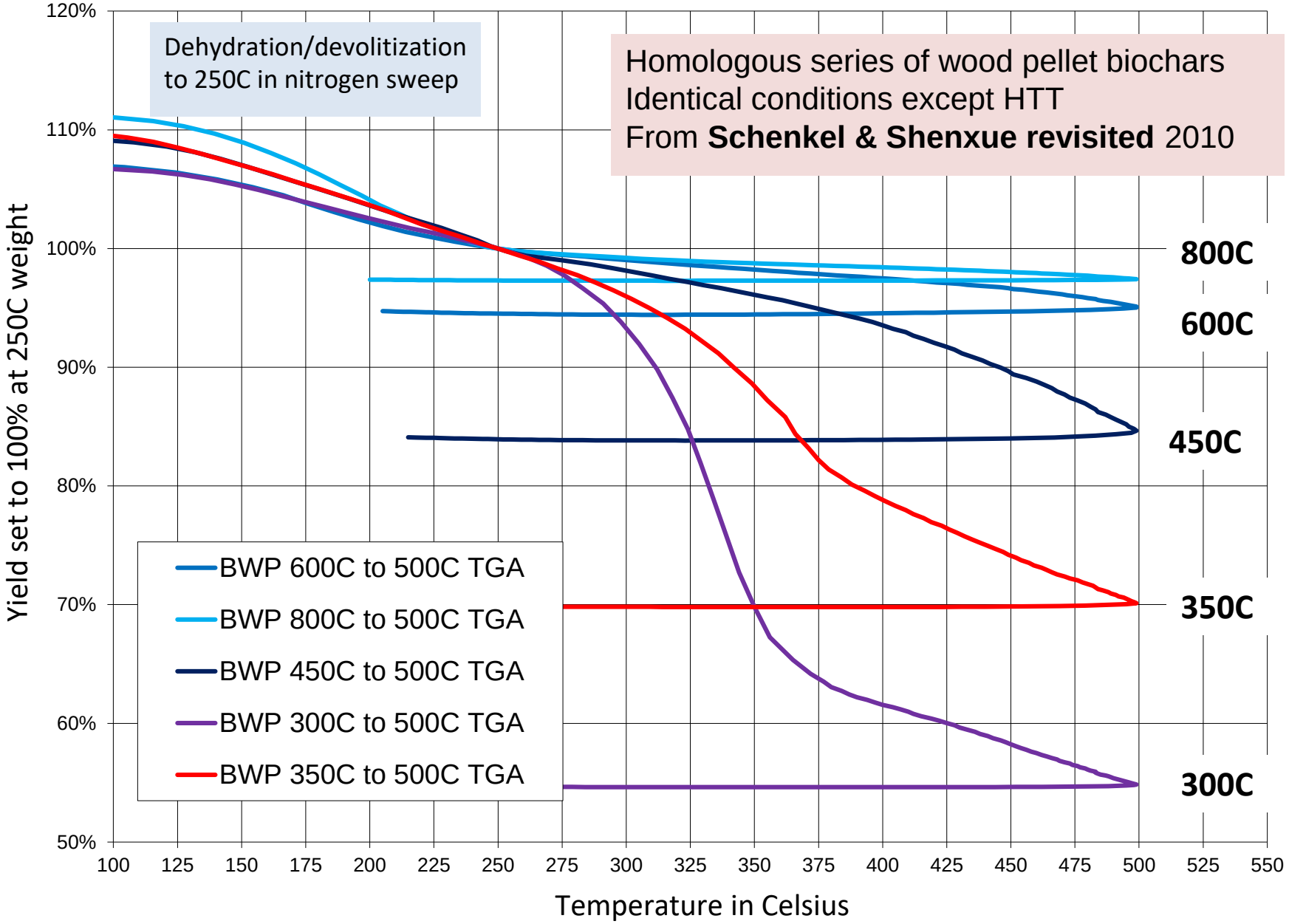
EBC uses an instrument for Proximate Analysis, specifying the Leco TGA 701

Most commercial labs offering Proximate Analysis use instruments since the labor cost is lower and calibration is easier. ASTM allows this alternative and IBI would likely not complain. **Cost: $30K to $40K**

Designation: D7582 – 15

Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis[1]

This standard is issued under the fixed designation D7582; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.



This is the kind of data a TGA collects – the entire temperature range and associated weight

From bulk properties to molecular census:

- The measurements up to now have been mostly simple measurements of bulk properties, with experimental challenges to tease out one portion from the composite.
- The ratio of H/C_{org} (Hydrogen to Organic Carbon atoms) was selected as the all-powerful discriminator of "Biochar-ness". **H/C_{org} of 0.7 divides the biochar world into *good* and *no good***
- Counting atoms requires instruments and instruments require calibrations and money to buy and operate.
- Instruments are great at creating answers with many significant figures, but do not and cannot measure the error in a specific measurement – that takes validation.
- **Instruments do what they are designed to do (literally go through the motions), but cannot modify what they see.**

H:Corg ratios for biochars vs biomass

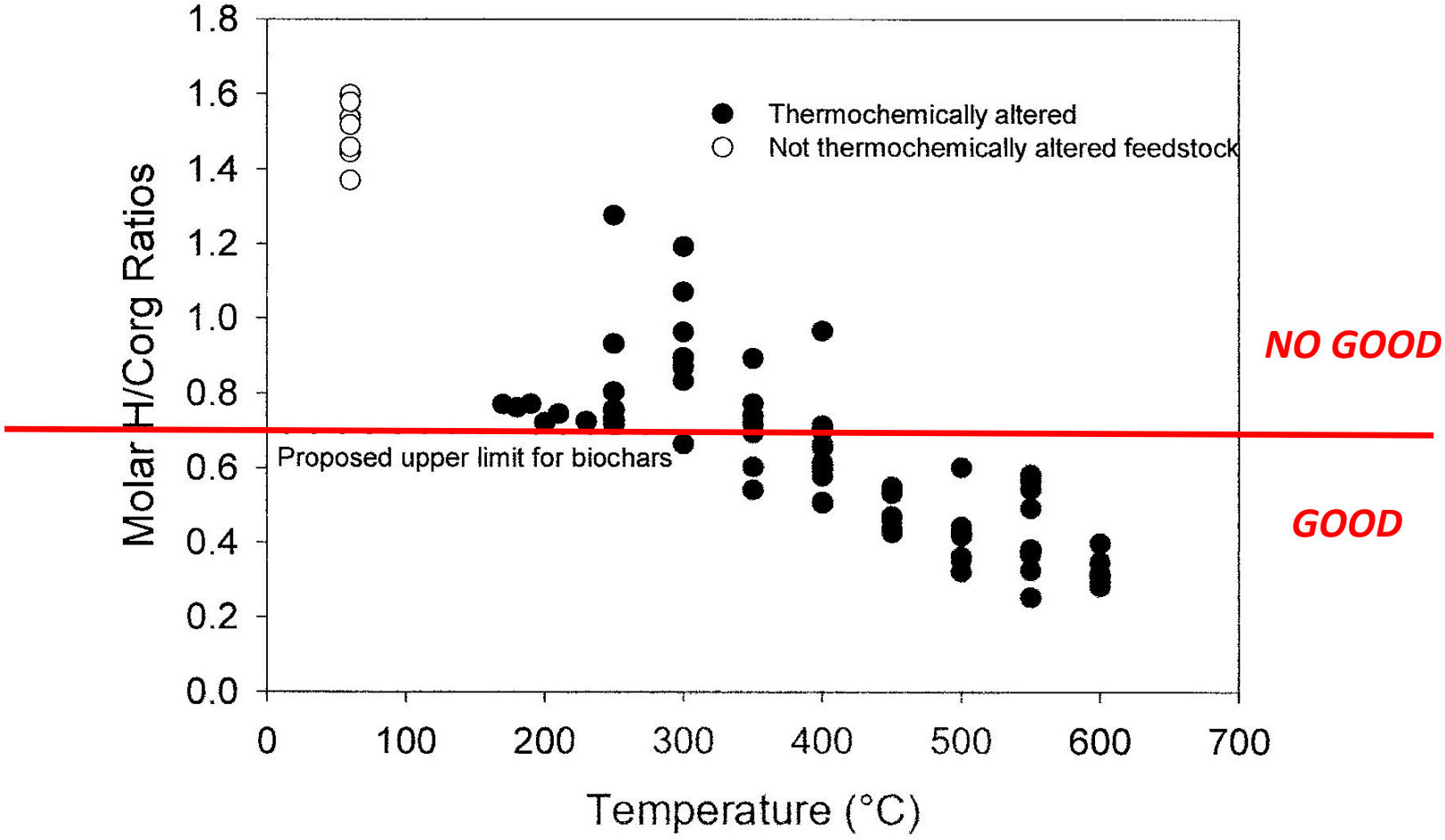


Figure A7.1. Relationship between molar H:C_{org} ratios and temperature of thermochemically altered organic matter in comparison to untreated biomass. The dashed line is the upper limit of 0.7. Data points below the 0.7 line are thermochemically altered materials that are considered to be thermochemically "converted" (data from Sevilla and Fuertes, 2009ab; Calvelo Pereira et al, 2011; Enders et al., 2012).

ASTM Internatrional (formerly American Society for Testing and Materials) has both **Methods**, which are a series of prescribed steps, and **Standards**, which discuss the overall utility of a method to one or more industries. One has to read many ASTM documents to accumulate all the advice for a given analytical challenge.

Designation: D3176 – 15

Standard Practice for Ultimate Analysis of Coal and Coke[1]

This standard is issued under the fixed designation D3176; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

NOTE 1—Moisture is not by definition a part of the ultimate analysis of coal or coke but must be determined in order that analytical data may be converted to bases other than that of the analysis sample.

NOTE 2—Inasmuch as some coals contain mineral carbonates, and practically all contain clay or shale containing combined water, a part of the carbon, hydrogen, and oxygen found in the products of combustion may arise from these mineral components.

For H/C_{org}, the closest ASTM method is D5373

Designation: D5373 – 16

Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke[1]

This standard is issued under the fixed designation D5373; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 Test Method A covers the determination of carbon in the range of 54.9 % to 84.7 %, hydrogen in the range of 3.25 % to 5.10 %, and nitrogen in the range of 0.57 % to 1.80 % in the analysis samples (8.1) of coal and of carbon in analysis samples of coke in the range of 86.6 % to 97.9 %.

Both IBI and EBC place great importance on H/C_{org}, with the H/C_{org} of any acceptable biochar being a maximum of 0.7 as a mole ratio. The C_{org} is calculated by measuring C_{total} and correcting it for C_{inorg} by this method.

Designation: D 4373 – 02

Standard Test Method for Rapid Determination of Carbonate Content of Soils[1]

1. Scope *

1.1 This test method covers the determination of carbonate content of soils and soft rock which can be readily broken down by mechanical effort. It is a gasometric method that utilizes a simple portable apparatus. Results should be clearly stated as the calcite equivalent in percent because different carbonate species cover a wide range of percent calcite equivalent as shown below for a number of carbonates:

So, the thing about ASTM methods is they are developed with industry input and are intended ONLY for the applications that were identified during the method development studies. Method development includes standard analytical techniques to validate the accuracy, precision and interlab reproducibility of the method for the identified and stated utility.

They are not like Chinese Menus, where one from Column A and one from Column B can be combined to meet the unique desires of the moment….

5. Significance and Use

5.1 This test method is used to determine the presence and quantity of carbonate in a soil specimen in terms of the calcite equivalent. The method is generally intended for use as an index of approximate carbonate content to assist with characterizing marine soils. Other test methods exist (such as Method C 25) to evaluate calcium carbonate equivalency for purposes of characterizing use of calcareous materials as soil modifiers or agricultural lining materials.

Note: C25 Methods are a better option for Carbonates quantification

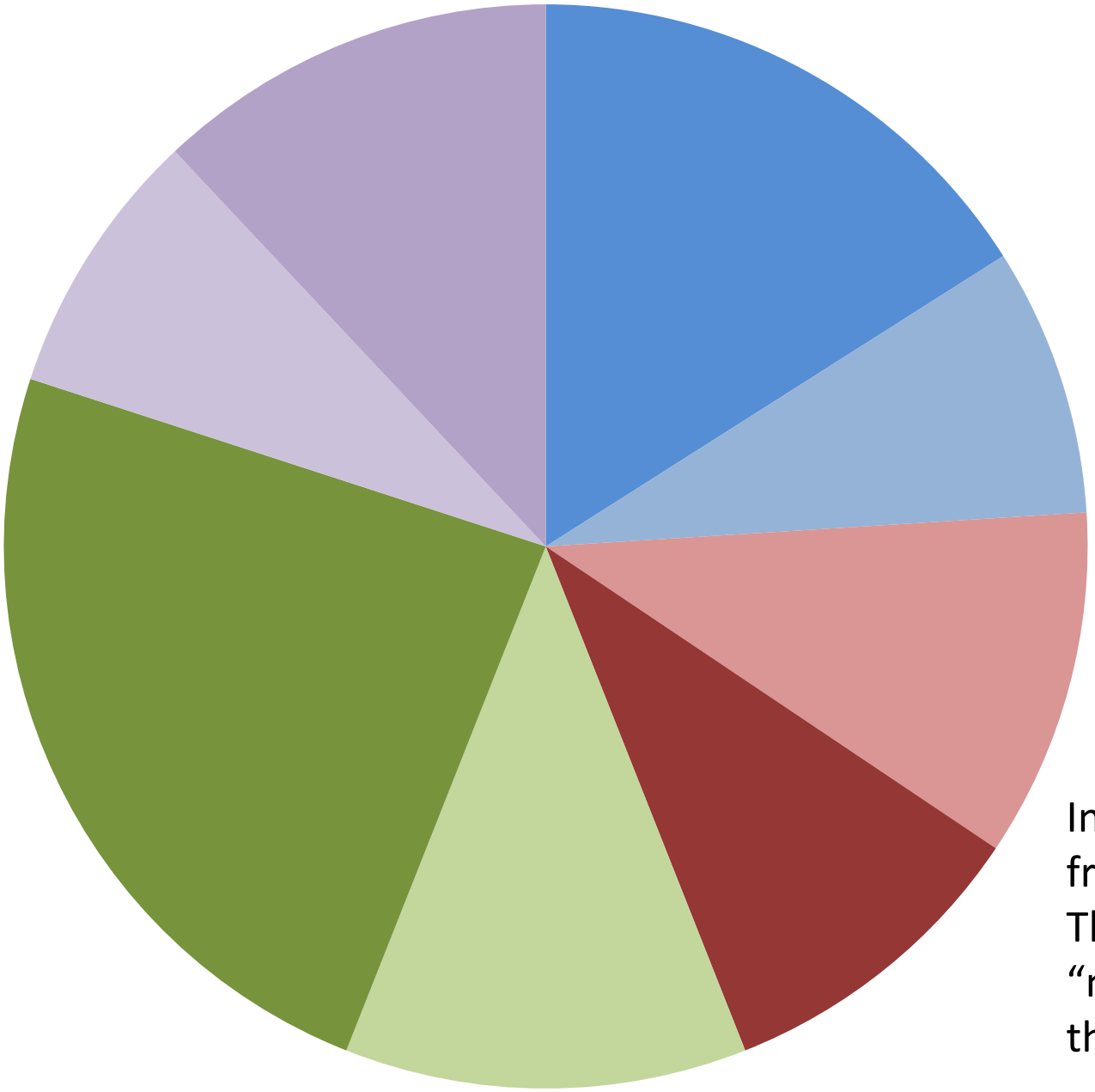
The Biochar 2018 paper, there was an analysis of how the errors in moisture and ash measurement could influence the H/Corg ratio. Since the slides are not yet available on the internet, the relevant portion is reproduced here.

NextChar

@Biochar 2018

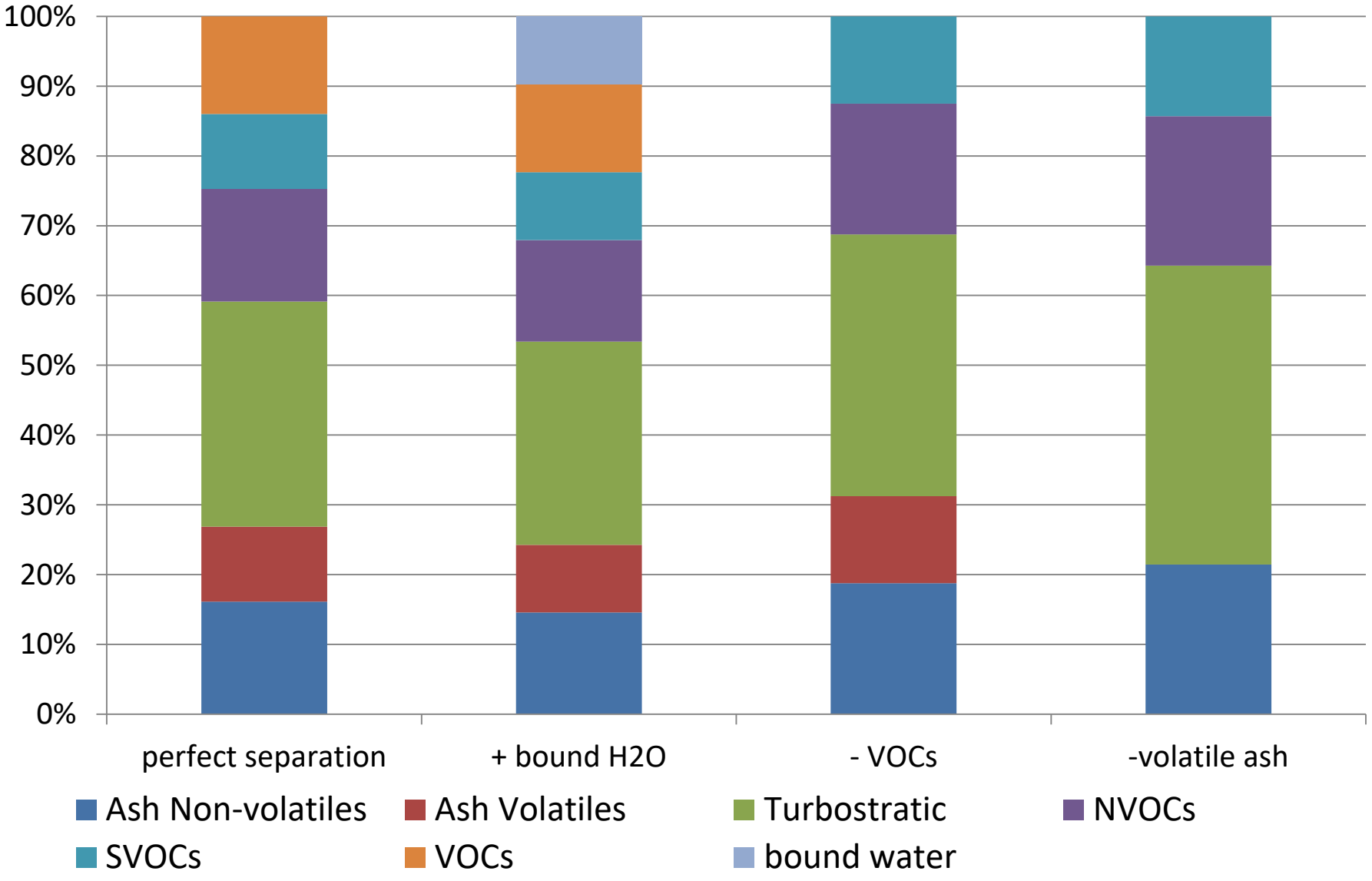
Biochar Standards and Characterization Schemes:

How and What is being measured, and What is it actually telling you

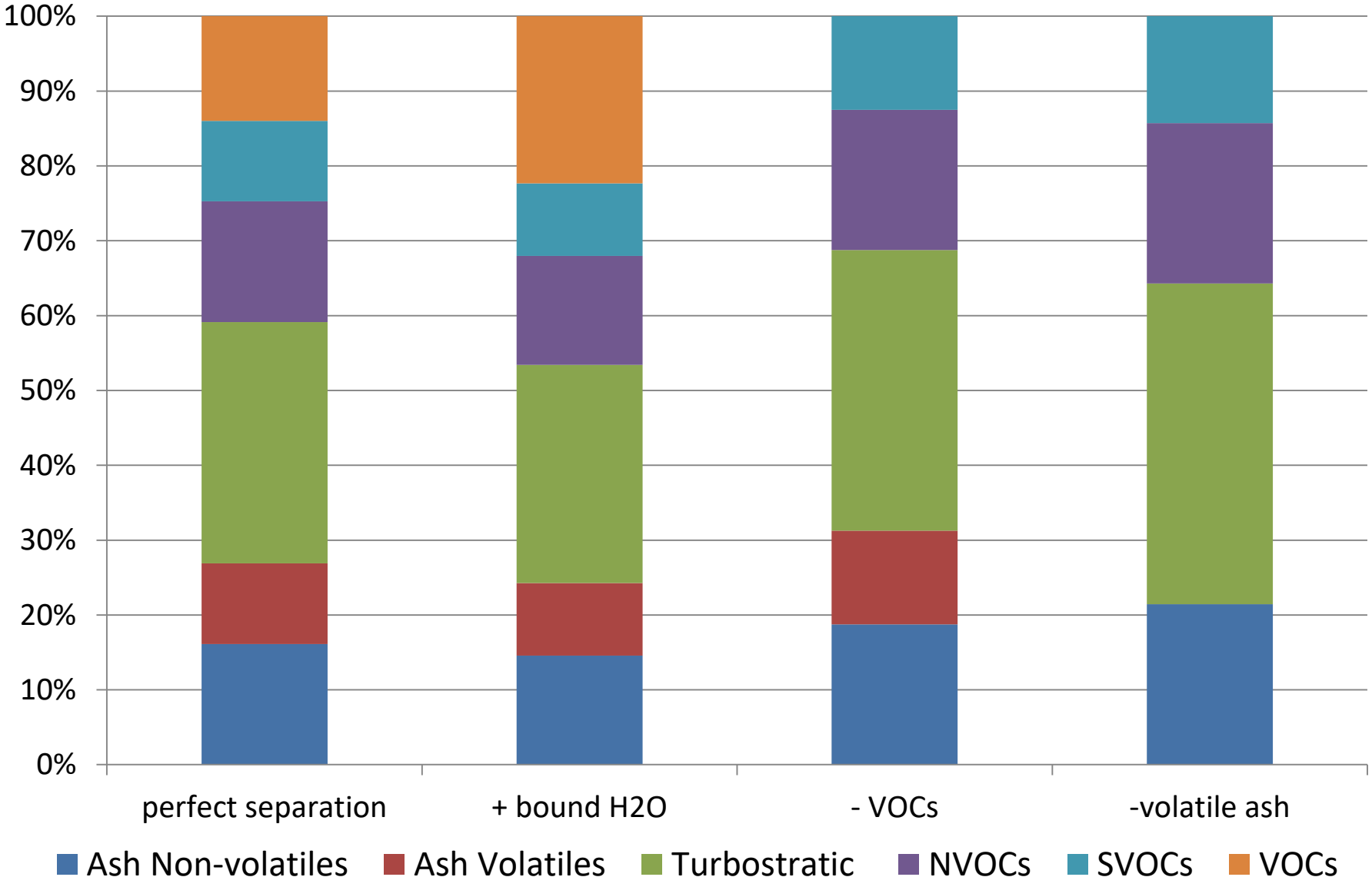


In this example, the free water is removed. The other classes get "melded" by errors in the analytical methods.

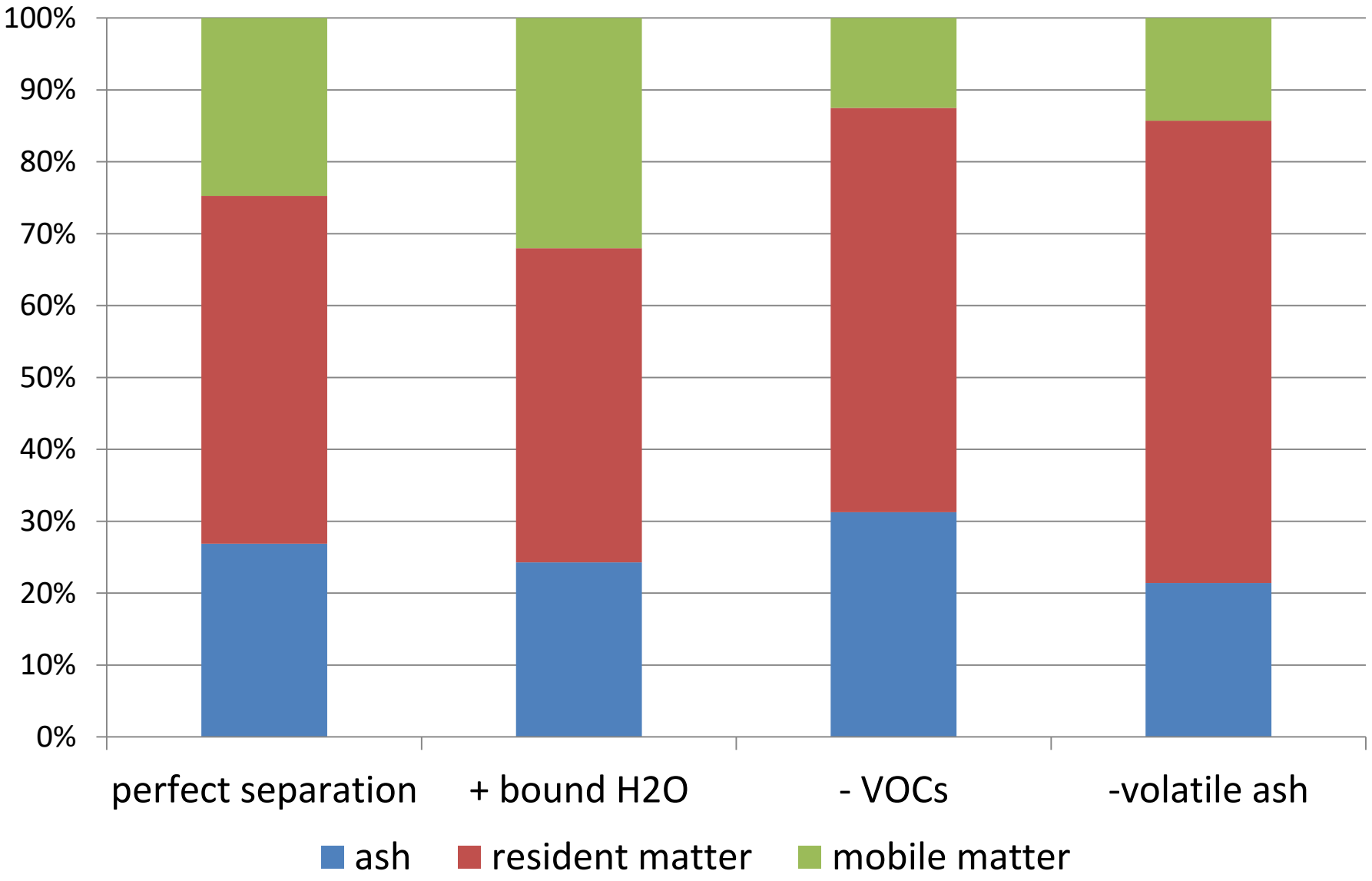
Let’s look at what errors in ash and water removal do to measured properties



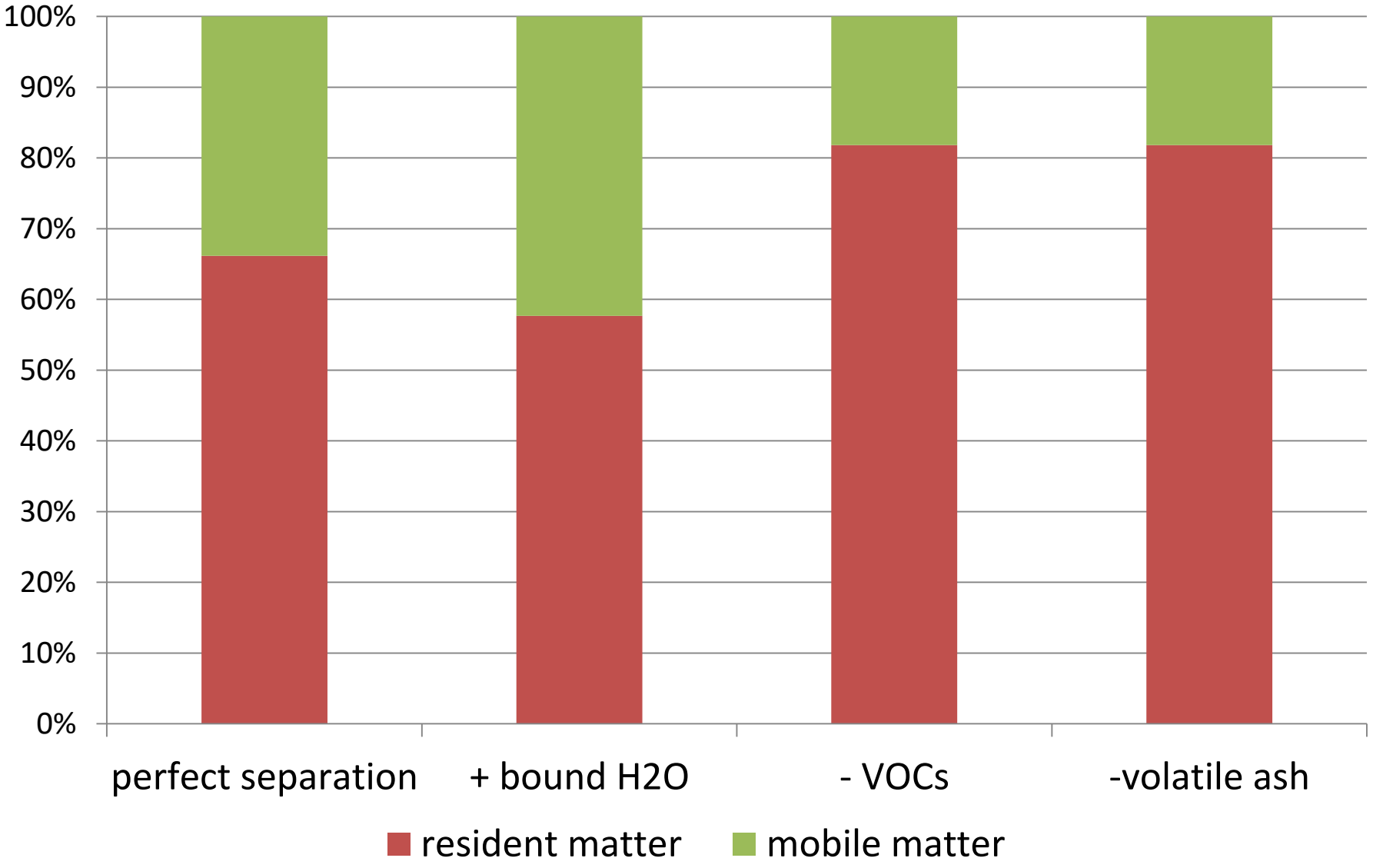
The residual water becomes Volatiles and the lost ash amplifies the other groups



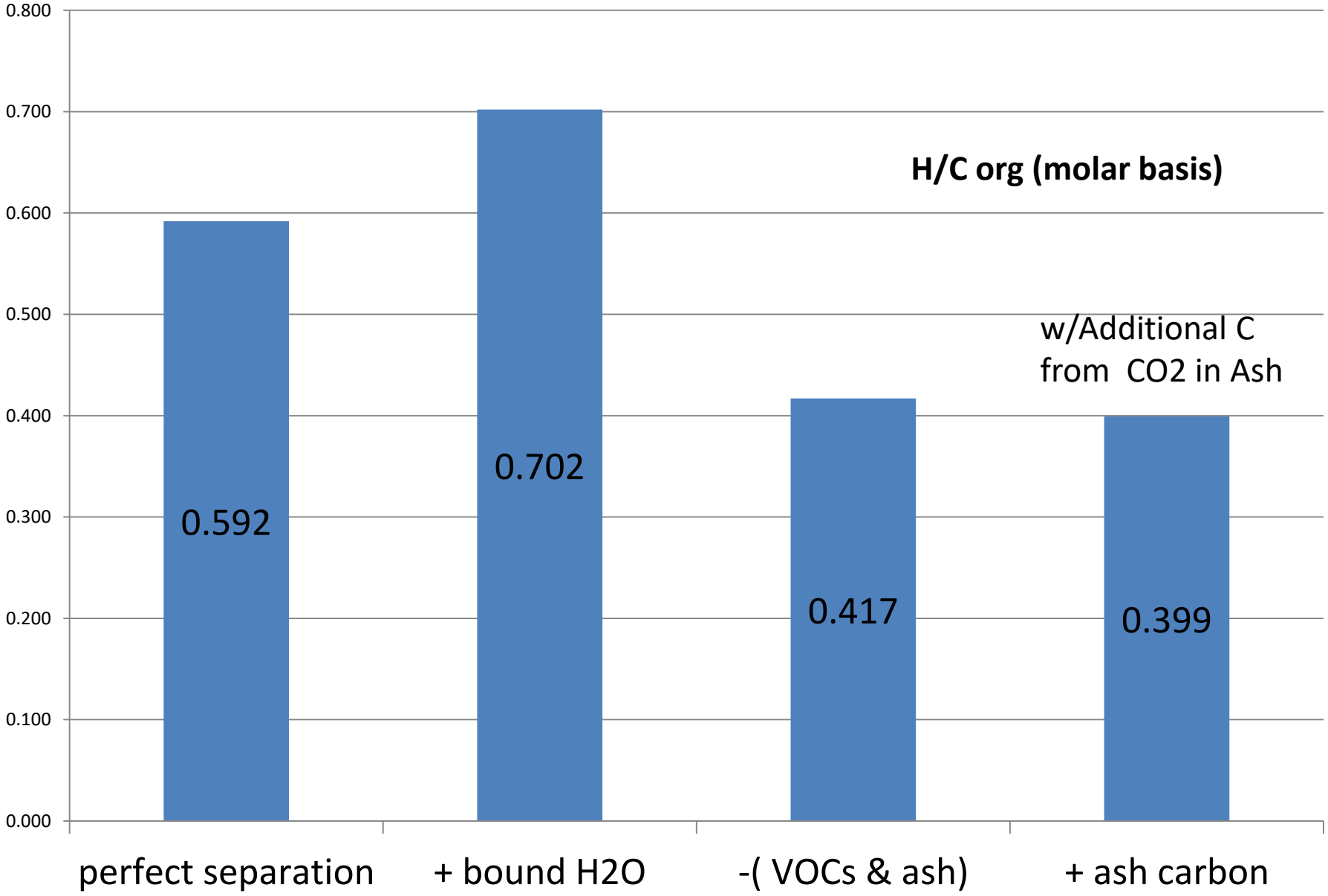
Clumping them back into the groups defined in the Proximate Analysis – less water



Normalizing by removing the ash portion, and assigning H & Corg to the organics



The errors introduced by inaccurate water and ash measurement bias the results



Additional information on the Baseline Biochar Metrics

- The Baseline Biochar Metrics consists of several documents, including
  - The BBM Procedures themselves,
  - Perspective on the BBM Procedures,
  - The comparison table of the EU vs IBI vs BBM measurements, and
  - BBM on a Budget – guidance on how to do the BBM with homemade equipment

Summary of the Conclusions

- Drying biochar is a compromise – it impacts all subsequent measurements and can ruin them if done improperly. Any drying of biochar removes VOCs and moisture together.
- Both IBI and EBC methods for Volatile Matter decompose ash carbonates and count them as VM; EBC counts them in ash also.
- C_{org} is calculated by C_{total}-C_{inorg}, where the C_{inorg} test is not quantitative. Unreacted carbonates are added to C_{org} .
- H includes any residual moisture, including inorganic hydrates, increasing H measurement from the CHNO analysis
- H/C_{org} accumulates all the errors of the prior tests.
- **Virtually all reported biochar characterization data suffer from excessive systematic errors due to the IBI/EBC protocols. *Most errors are easily avoided with proper analytical methods.***

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Options for Characterizing Biochar and Evaluating Quality

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July 2, 2019