Integrating the thermal behavior and optical properties of carbonaceous aerosol

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Motivation/Project Philosophy
(repeat from Year 1)

- Need to understand existing & incoming data
  - Like it or not, data are widely used!
  - Approaches developed *must* be applicable on retrospective basis
- “Artifacts” might be interpretation opportunities
  - Take advantage of wealth of data in optical & thermal traces
- No method is “right” or “wrong”
  - Different optical+thermal responses observed
  - Hope: results of any methods can be interpreted on common ground

Outline

1. Reactor Model
2. Light-absorbing carbon optics
3. Pyrolysis/charring
4. Can kinetics help?
5. Back to the model
6. Recommendations

Definitions:
“native LAC” = particles that absorbed light when deposited on filter
“pyrolytic carbon” = PC = material that pyrolyzed during analysis
“organic carbon” = OC = other non-carbonate carbon

Reactor model for TOA (I)

<u>Each "artifact" can be summarized thus</u>:

- *Analysis does not account for co-evolution of different types of carbon.*

  (So let's account for it!)

- *System has two outputs:*

  carbon (FID) and absorption (ATN)

- *<u>Required</u>: only 2 types of carbon evolving simultaneously.*

Formal reactor model for TOA

$$\vec{y} = \begin{bmatrix} \Delta FID \\ \Delta ATN \end{bmatrix}$$

System response

System state

$$\vec{x}_n = \begin{bmatrix} OCc \\ OCn \\ PC \\ LAC \end{bmatrix}$$

could have 5 (shown later)

$$\vec{y} = \mathbf{R}\Delta\vec{x}$$

Transfer function

$$\mathbf{R} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ K_C\sigma_C & K_N\sigma_N & K_P\sigma_P & K_L\sigma_L \end{bmatrix}$$

Source of the "problem"

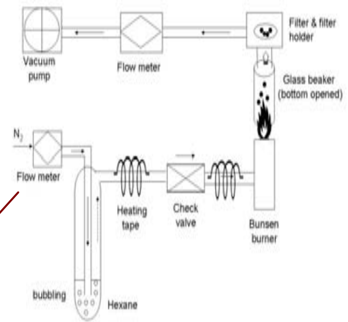
Carbon

Optics

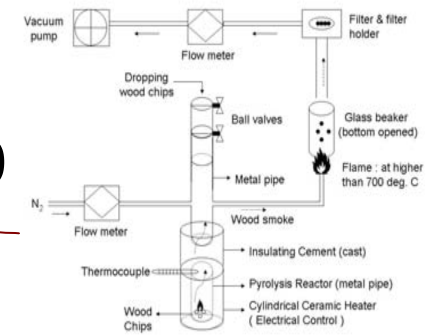
$$\begin{bmatrix} FID \\ \Delta ATN \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ K_C\sigma_C & K_N\sigma_N & K_P\sigma_P & K_L\sigma_L \end{bmatrix} \Delta \begin{bmatrix} OCc \\ OCn \\ PC \\ LAC \end{bmatrix}$$

- Two equations, four unknowns
  - Need more constraints!
- Default approach: assume yields
  - used in present TOA

We explore controlled & source samples



N	Description
71	Hexane soot (lab generated)
50	Model compounds (some ~water-soluble)
55	Wood combustion (lab generated)
50	Wood combustion (cookstoves)
136	Diesel vehicles (DIESEL project, Bangkok)



1. Reactor Model

ΔATN vs carbon mass

The short story: Differentiate the laser signal.

The long story:

Transmittance of clean filter

Enhancement by collection on filter

$$100 \ln \frac{I}{I + \Delta I} = \sum_{n=1}^{N} K \sigma_{abs,n} \Delta L_n$$

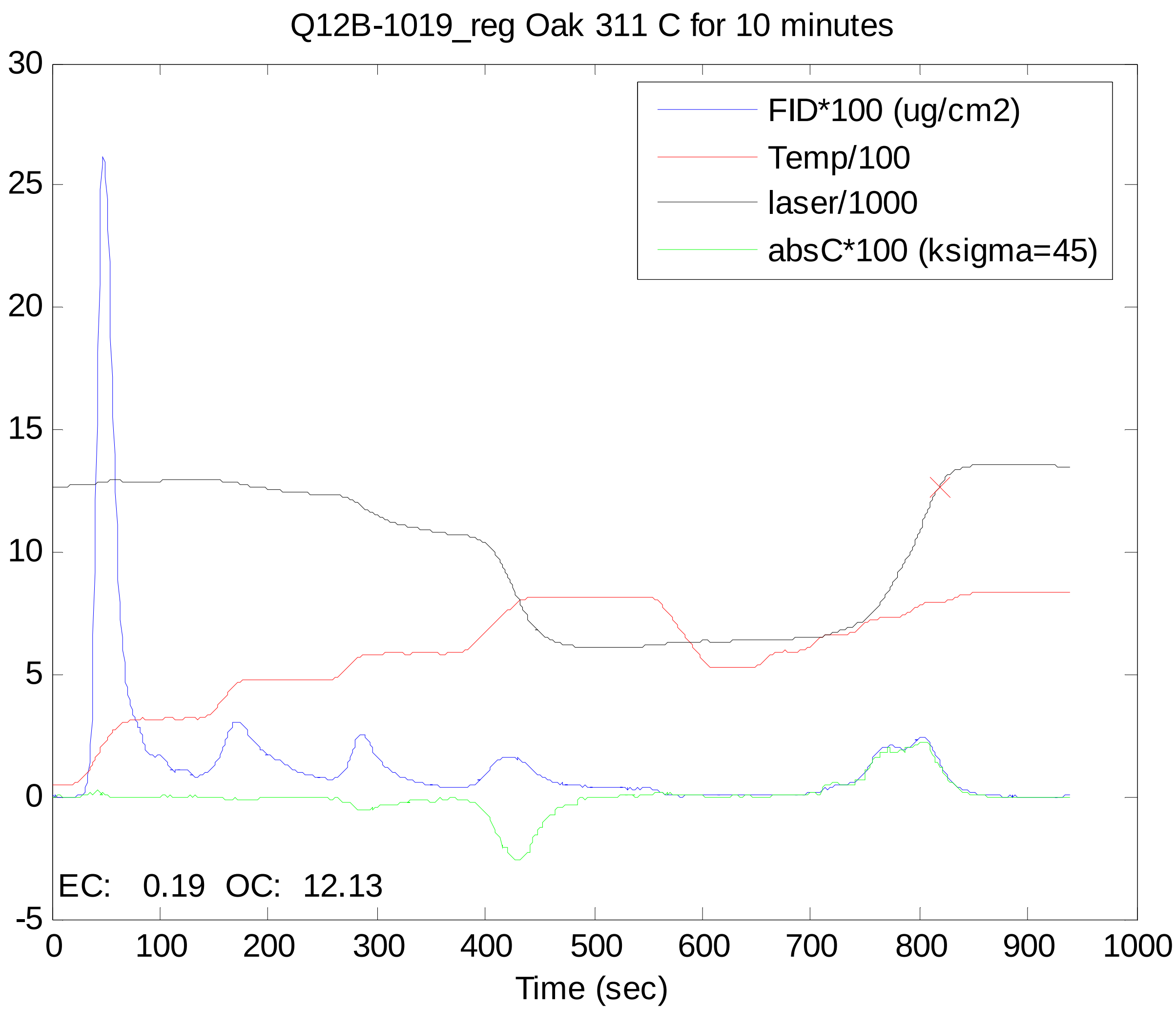
Loading of species I ($\mu g/cm^2$)

Transmittance of loaded filter

Absorption cross-section of suspended species I (m^2/g)

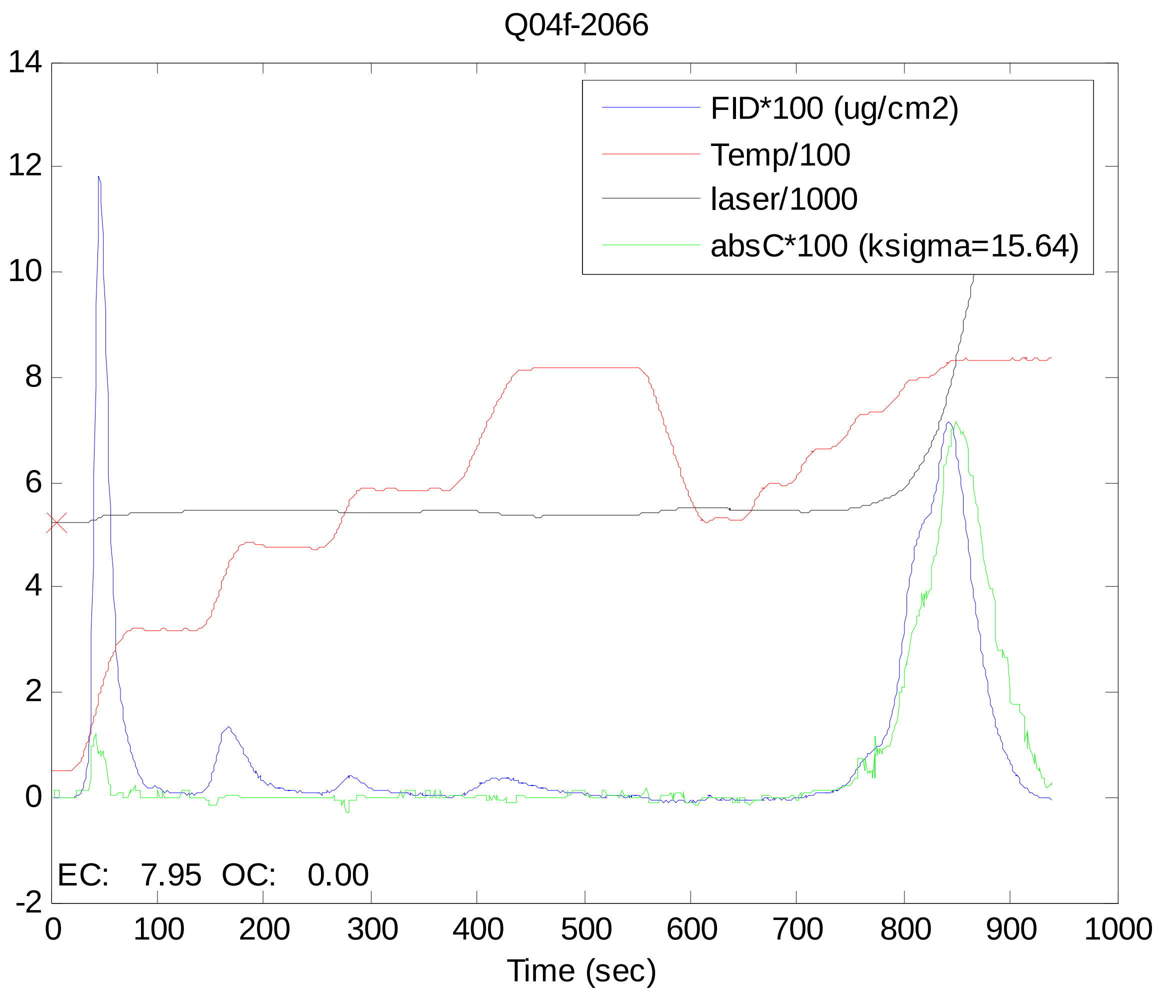
Examples to follow…

Smoldering woodsmoke "thermabsgram"



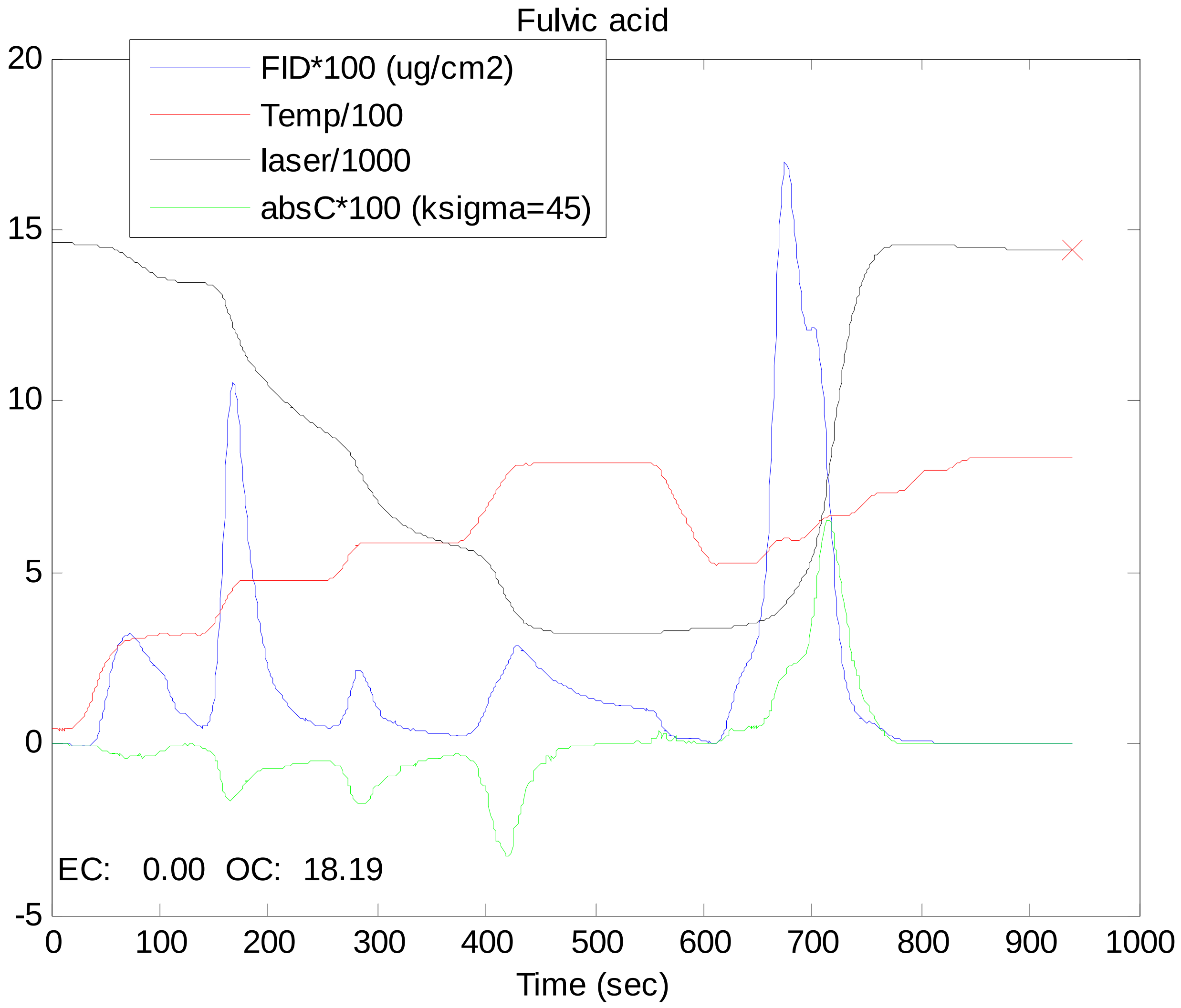
2. Optics

Diesel thermabsgram



2. Optics

Fulvic acid thermabsgram



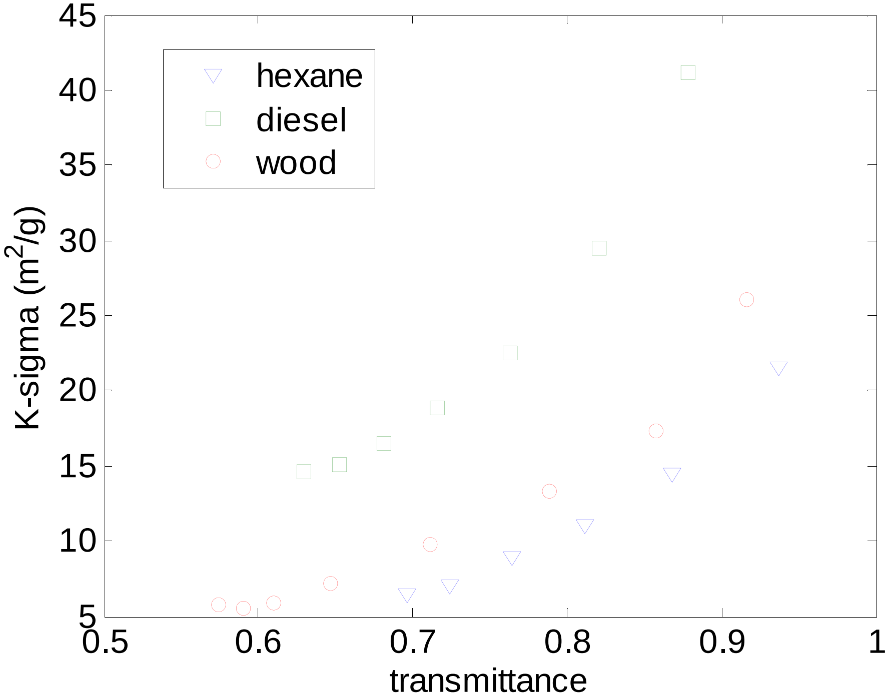
2. Optics

All black carbon is not created equal
(despite Bond & Bergstrom, 2006)

$$100\frac{d\ln I}{dL} = K\sigma_{abs,n}$$

K (enhancement) varies with:

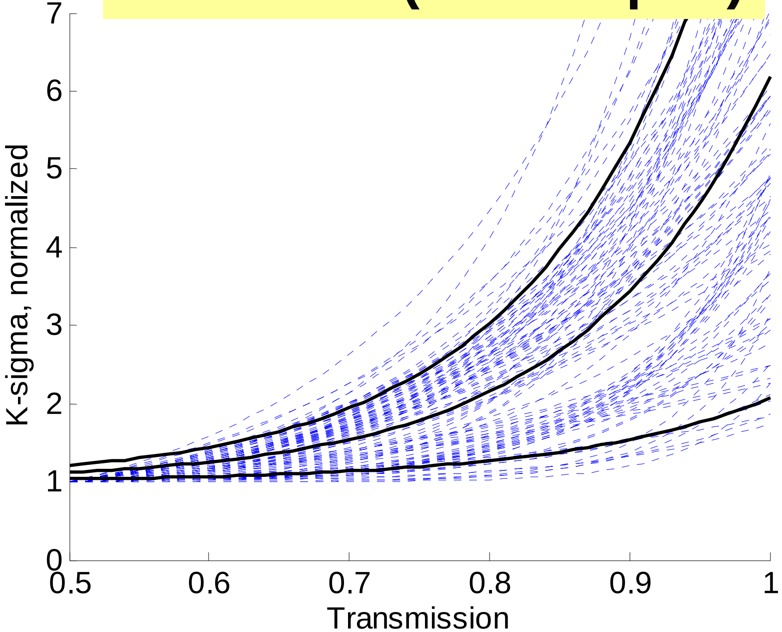
- source type
- filter transmittance
- mood



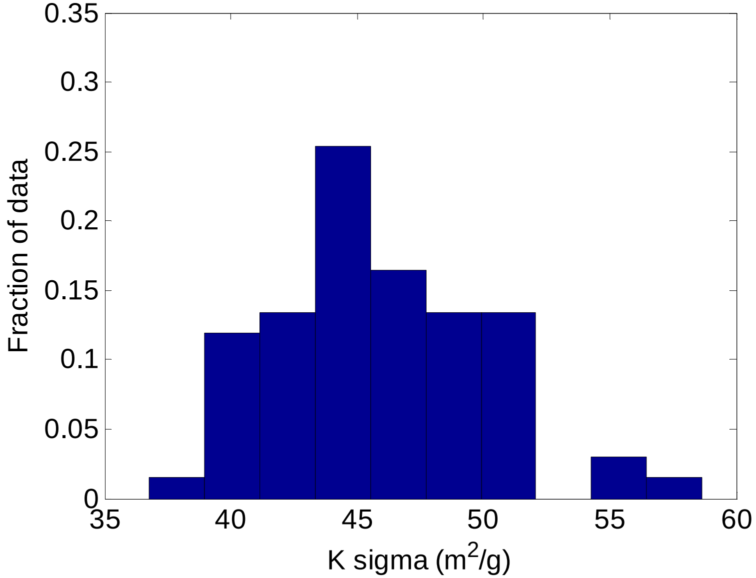
p<0.0001 (hexane-diesel-wood)

K-σ differs between native LAC & pyrolytic carbon

Native LAC (101 samples)



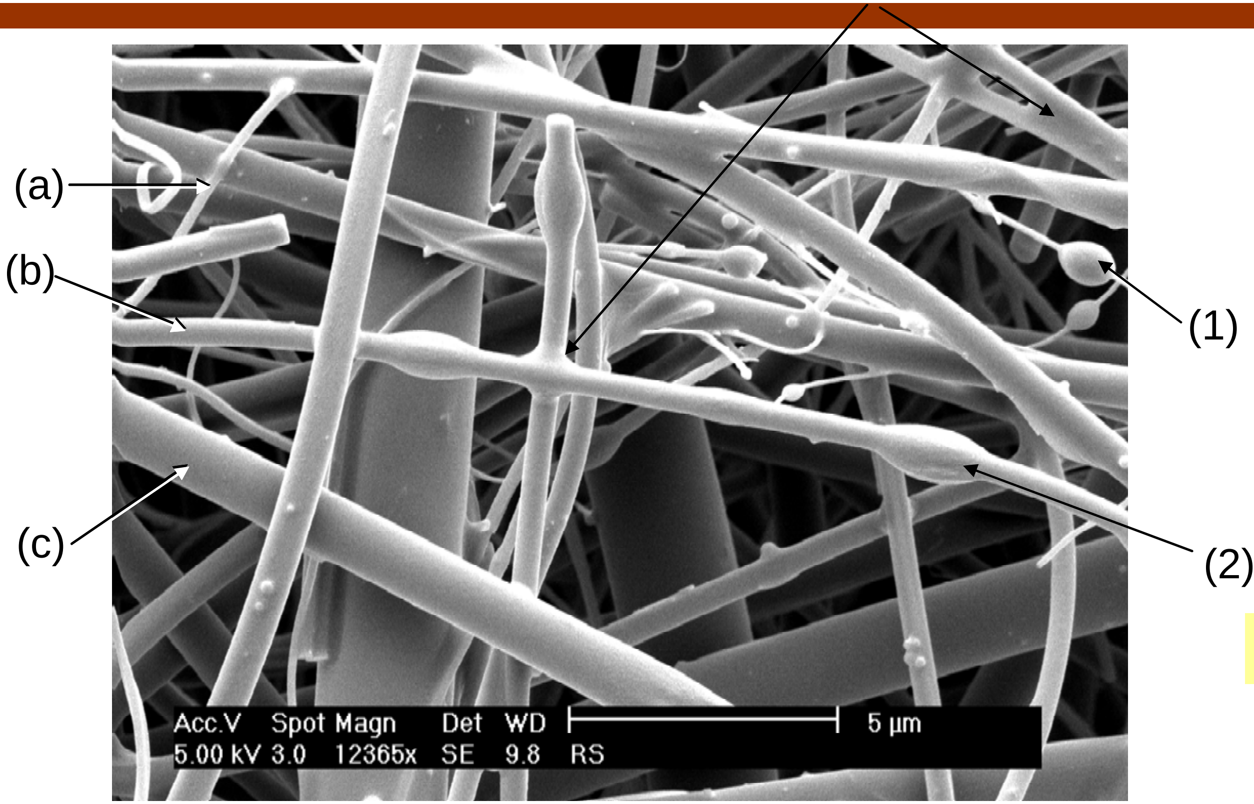
Pure pyrolytic carbon (PC)



We knew that.
(Chow et al. 2004;
Subramanian et al. 2006)

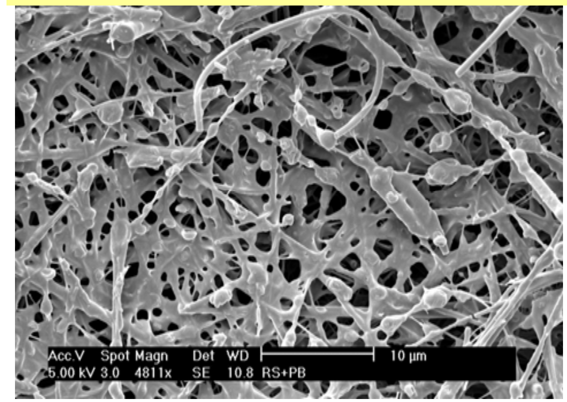
2. Optics

Charrable carbon is liquid on filters

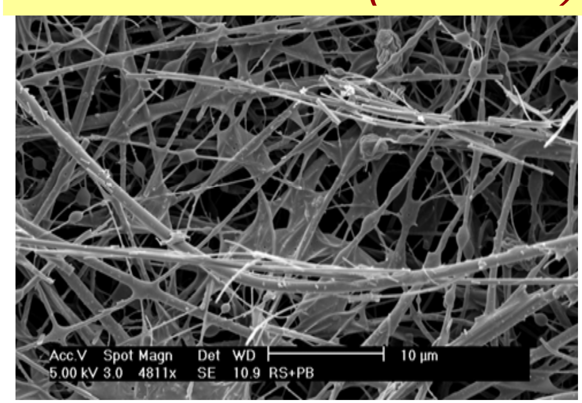


- Shapes are consistent with droplet-on-fiber theory
- Implies that most OC is present as fiber coatings

Rice straw burning (Thailand)



Wood cookstoves (Honduras)



2. Optics

Subramanian et al., 2007

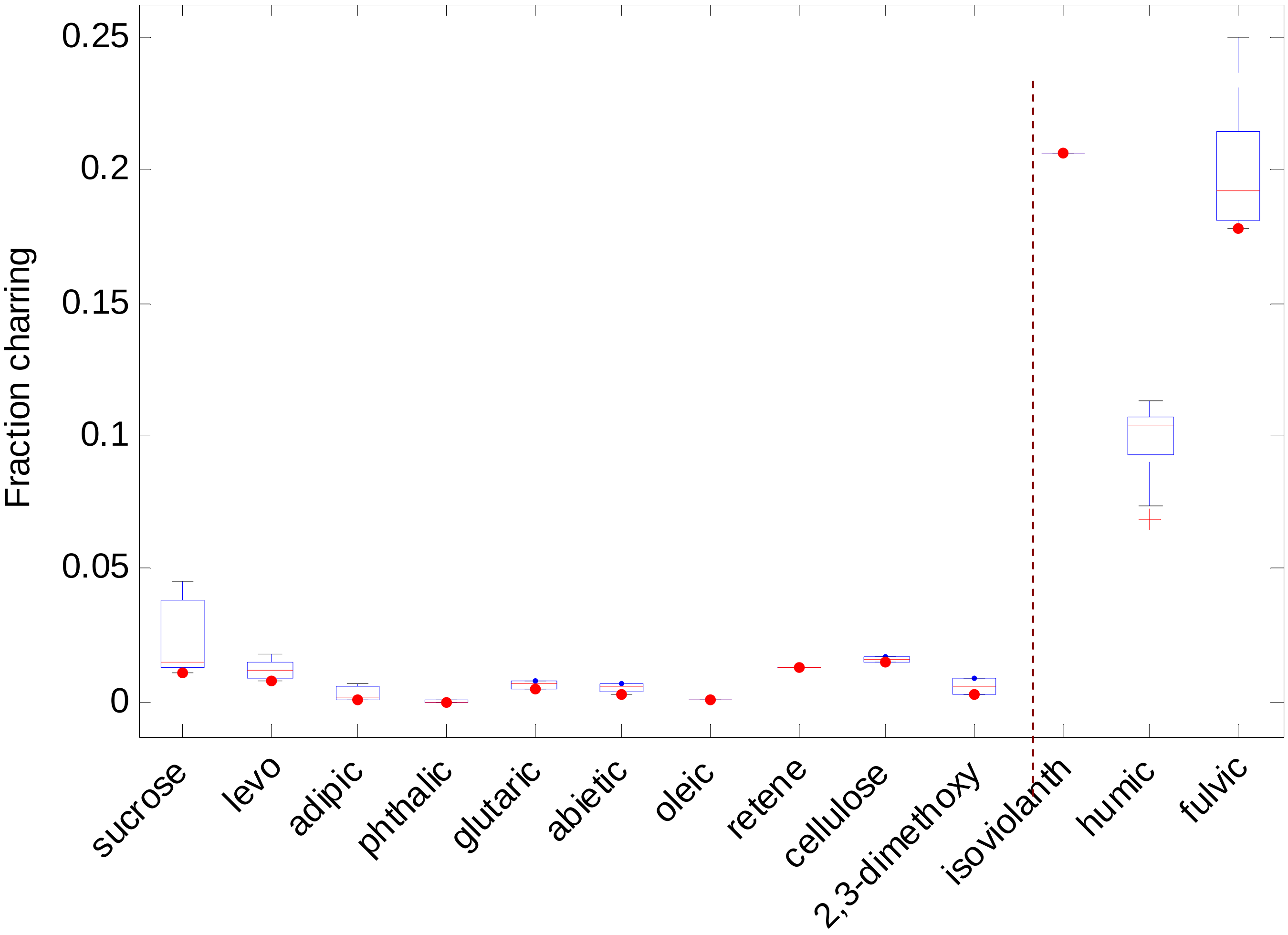
Optics summary

- ATN-to-carbon ratio depends on carbon type and filter loading (transmittance)
- PC-ATN and LAC-ATN differ & can be used to distinguish the two
- Repeatability of individual results is limited

What does charring indicate?

- Water-soluble extracts char (Yang and Yu, 2002)
- Methanol removes most of charring (but not all) (Subramanian et al, 2007)
- Biologically-derived and complex molecules char (Cadle et al, 1980)

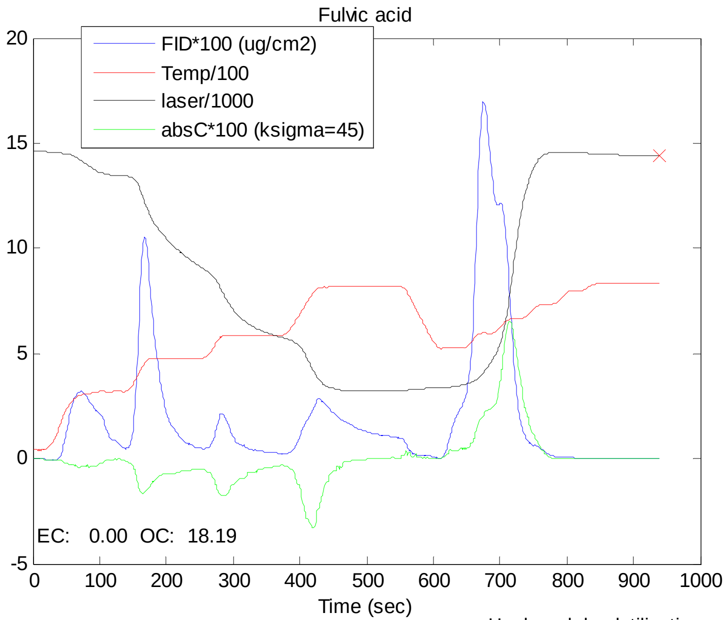
Most model compounds don't char

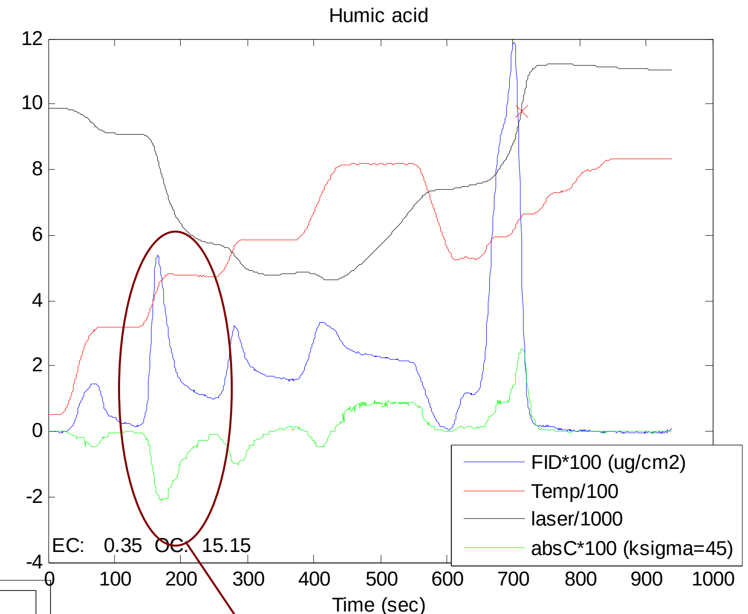


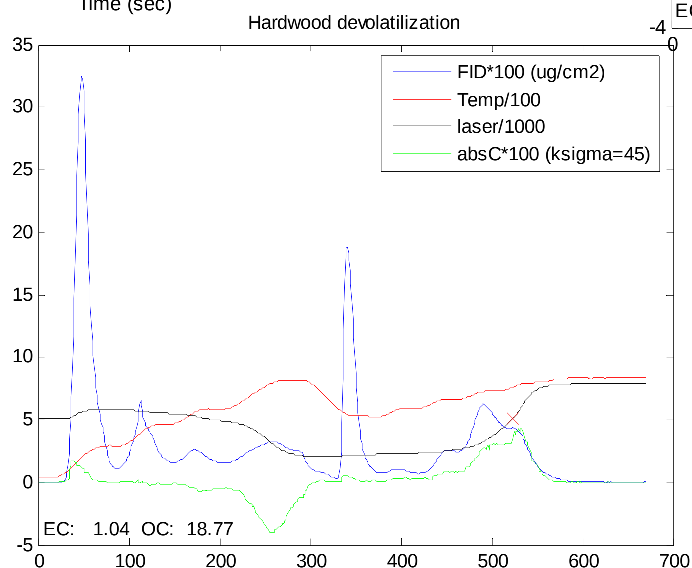
...not even water-soluble compounds!

3. Charring

Complex compounds do char



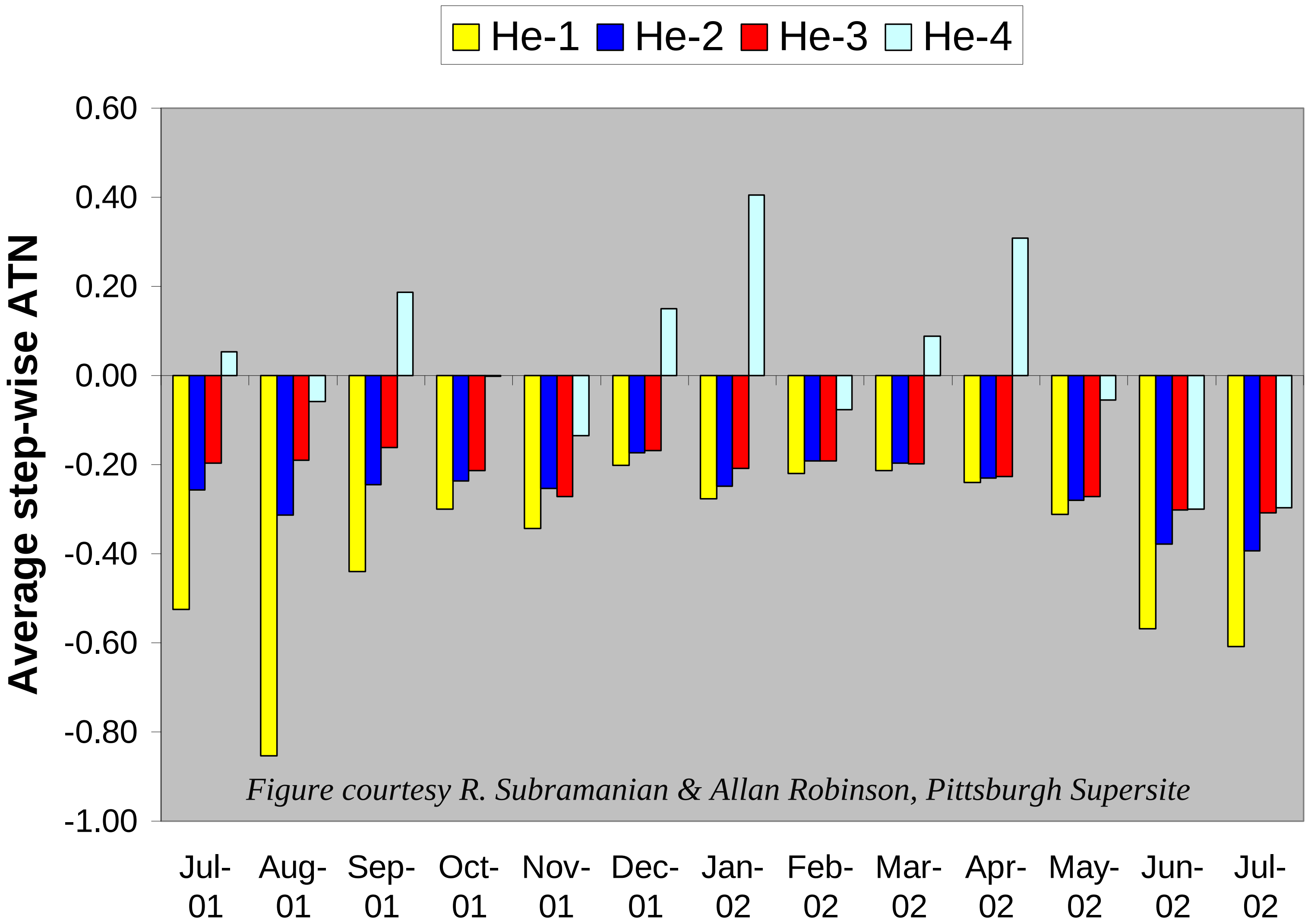




"Early charring"

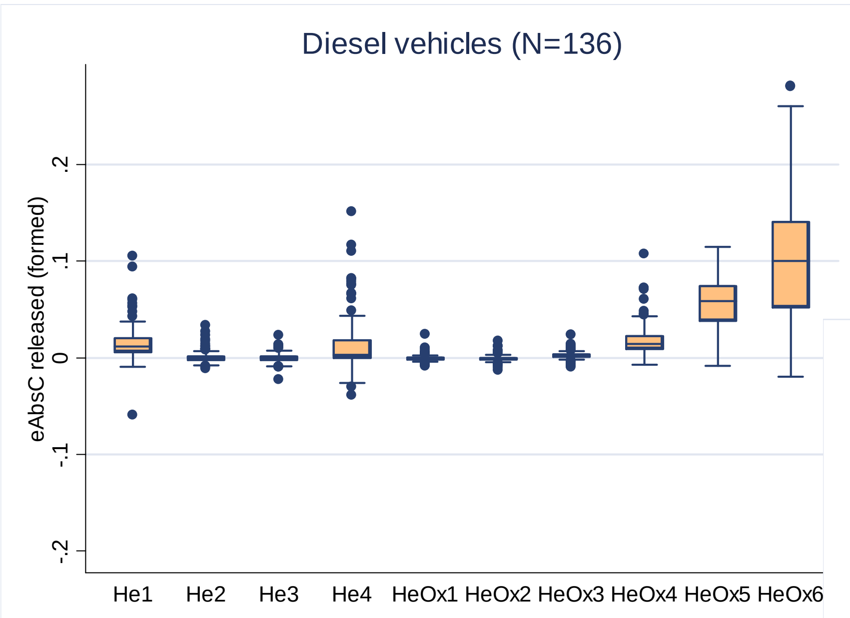
3. Charring

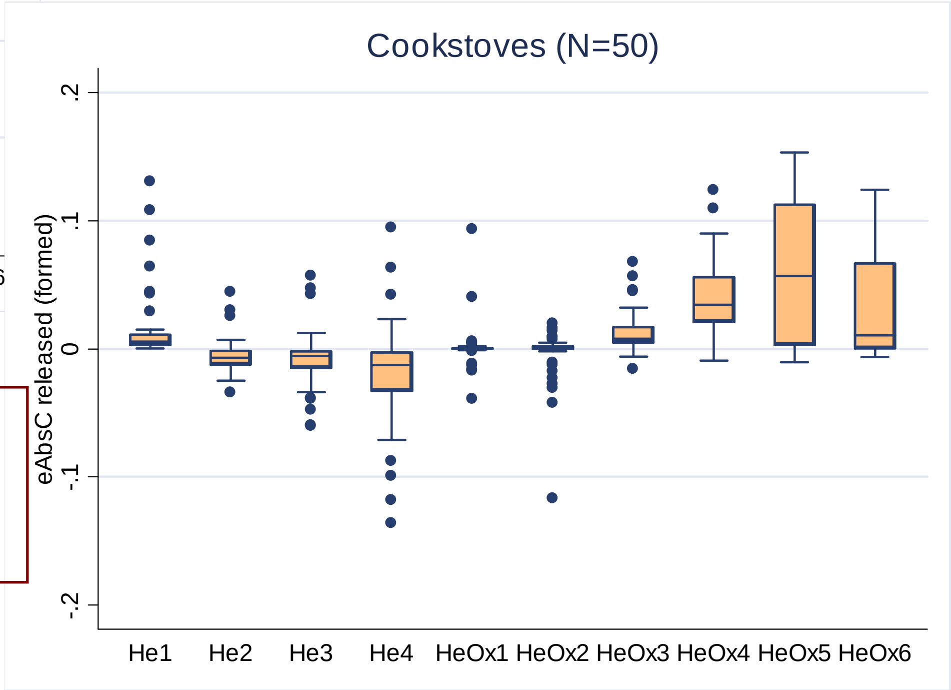
Where does “early charring” come from?



3. Charring

…Not from sources!

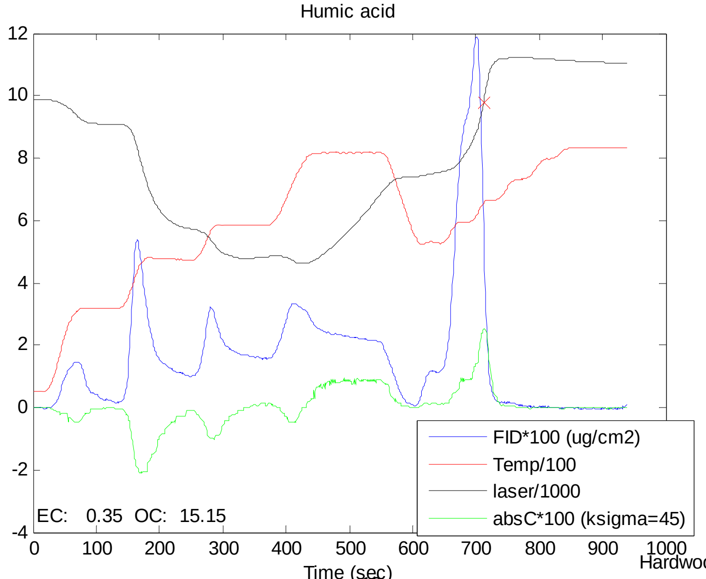


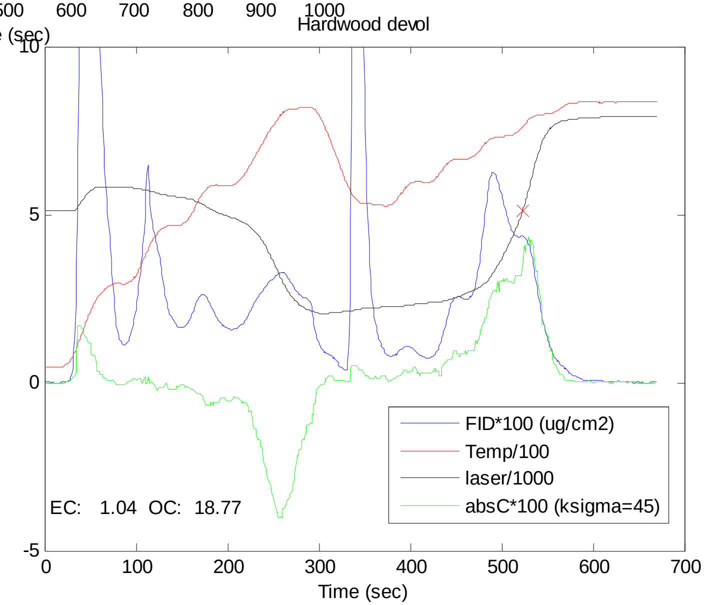


Review of pyrolysis mechanisms says: polymerized material+ catalysis→ further polymerization = charring

3. Charring

Two equations, three unknowns…





Released in He-4:

PC, LAC

(if oxygen present)

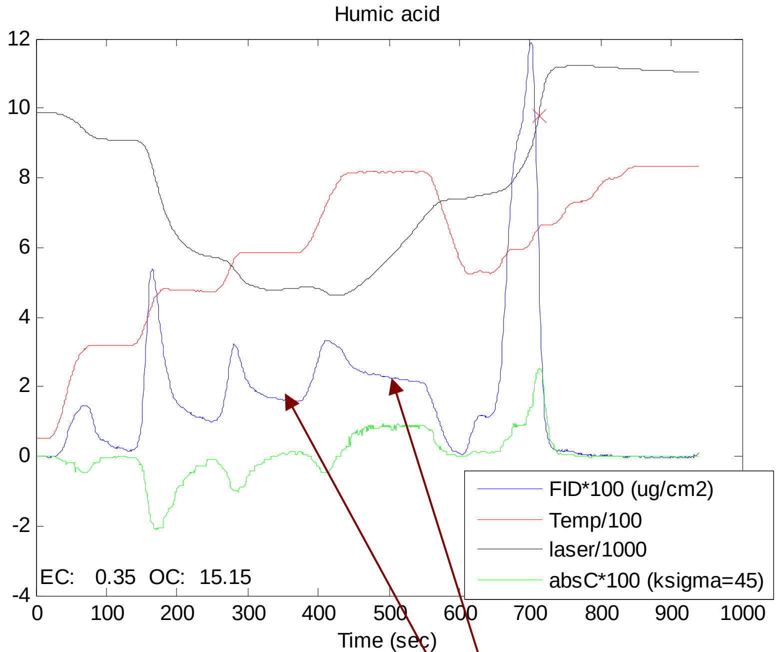
OC

Released in “early” HeOx:

OC, PC, LAC

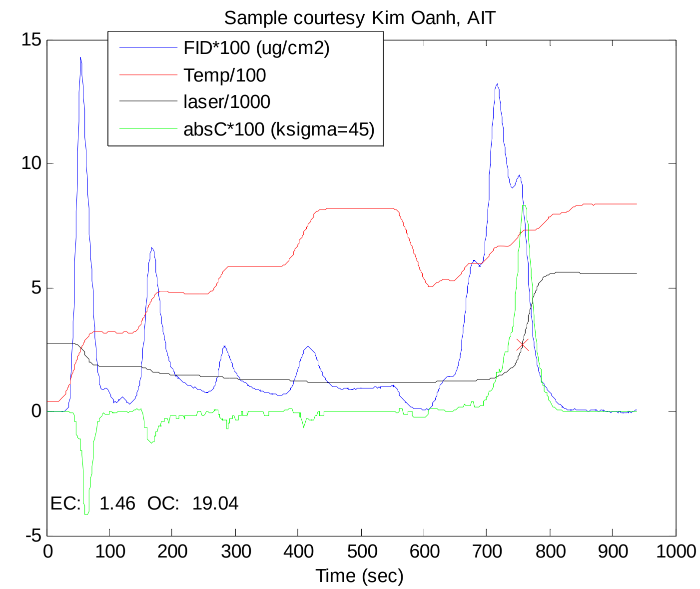
4. Kinetics?

Oh, that heavy OC…



Plateau =
slow volatilization

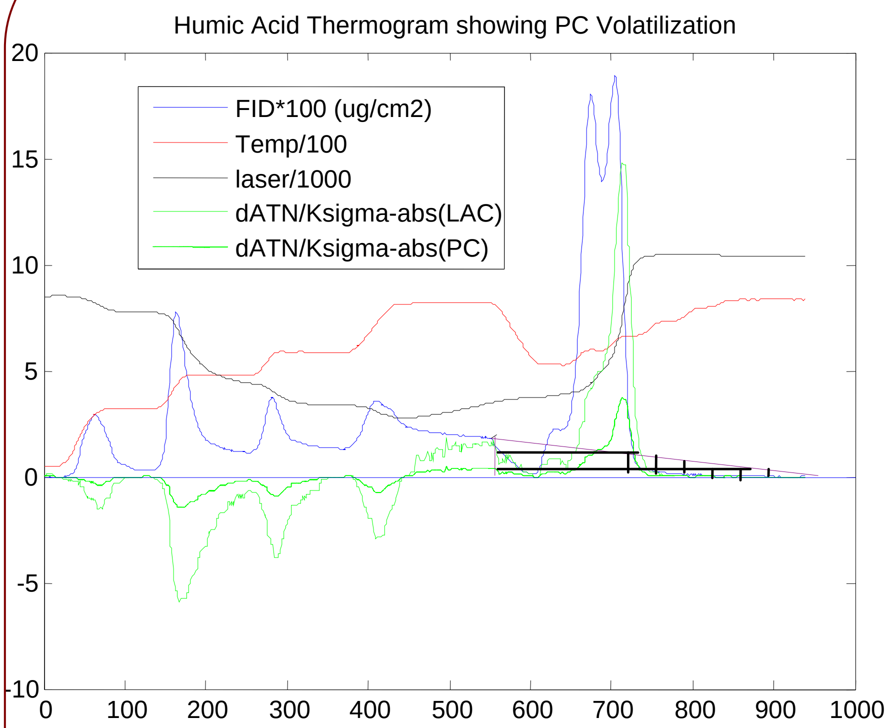
- Simple view: 2 mechanisms
  - Decomposition/ volatilization
  - Slow volatilization

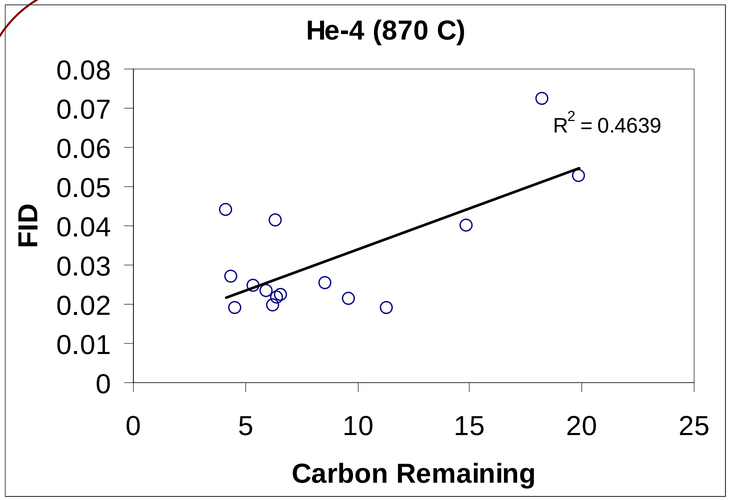


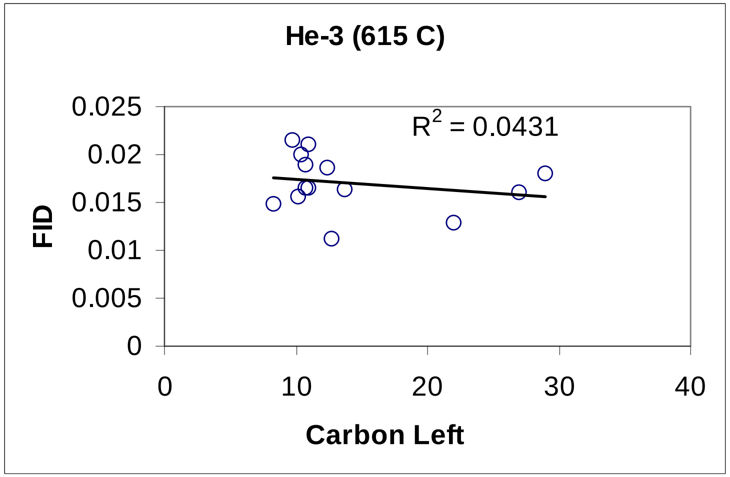
4. Kinetics?

Idea: Infer heavy OC from traces

Method 1 (Projection)







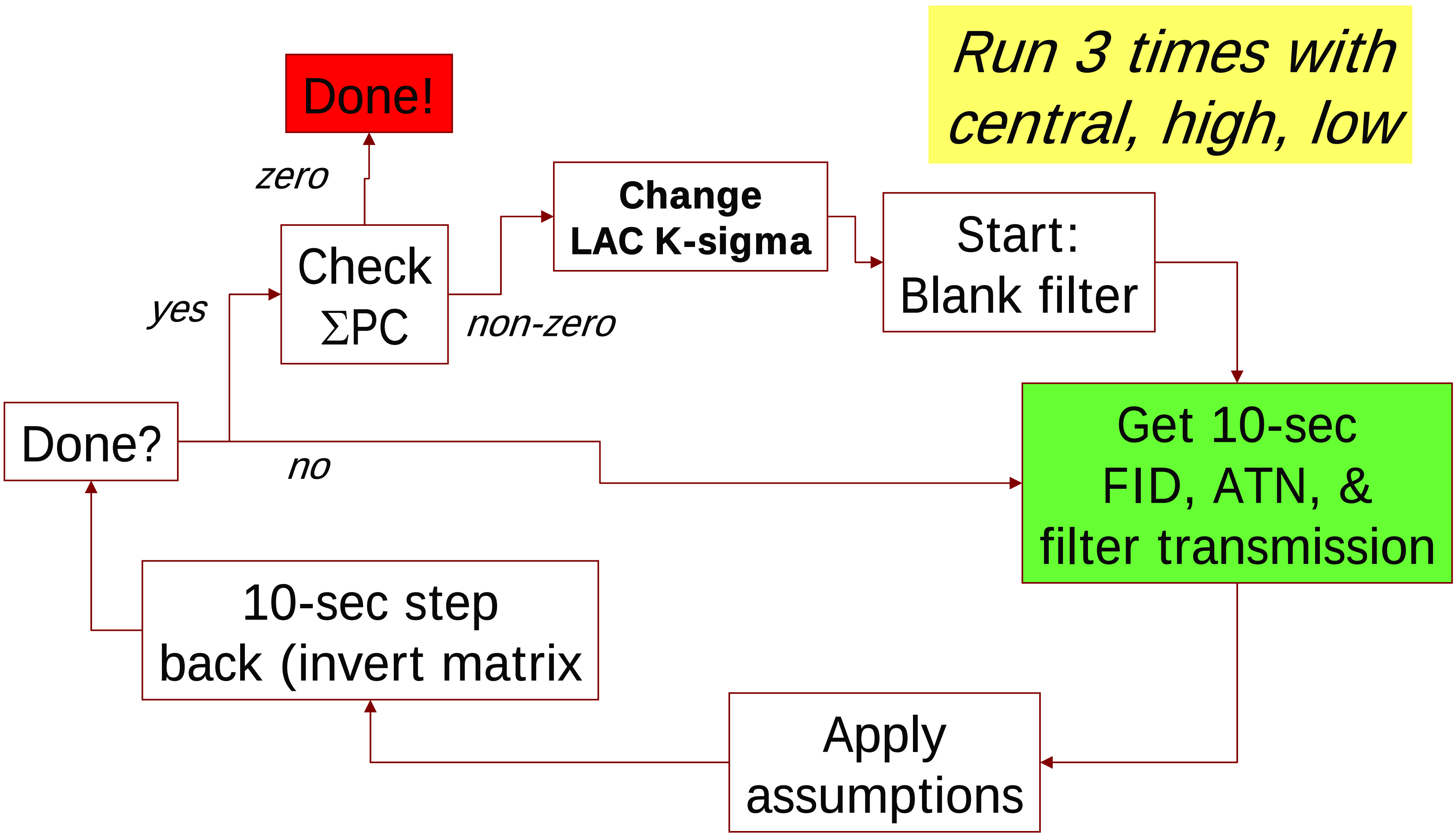
Method 2 (kinetic)

4. Kinetics?

Kinetics summary

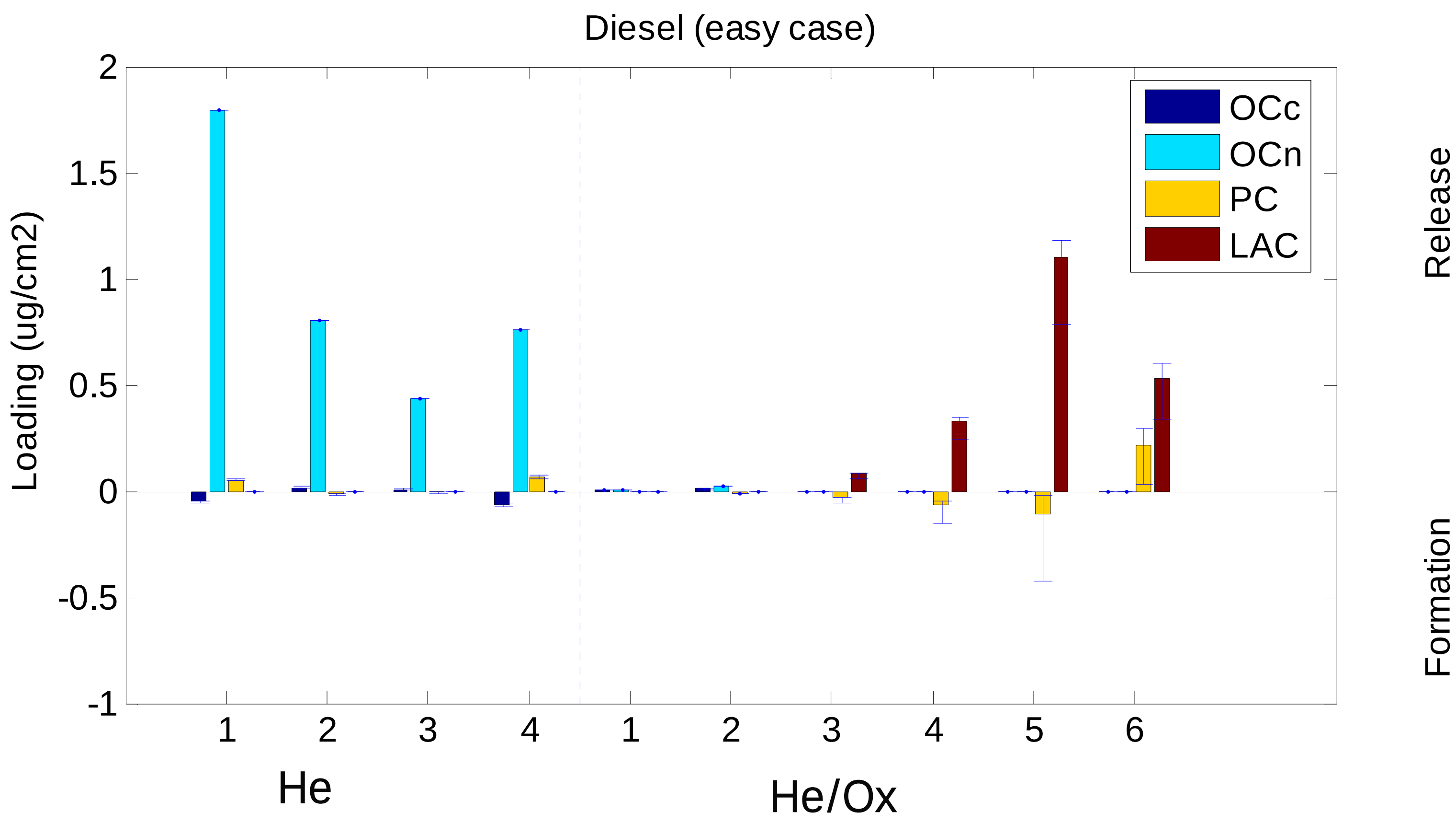
- Tried *many* approaches using kinetics to draw inferences.
- While punches from identical sample are reproducible, even “similar” samples aren’t.
- Statistical approach (as for optics) seems to be the only possibility.

(Today's) Reactor model



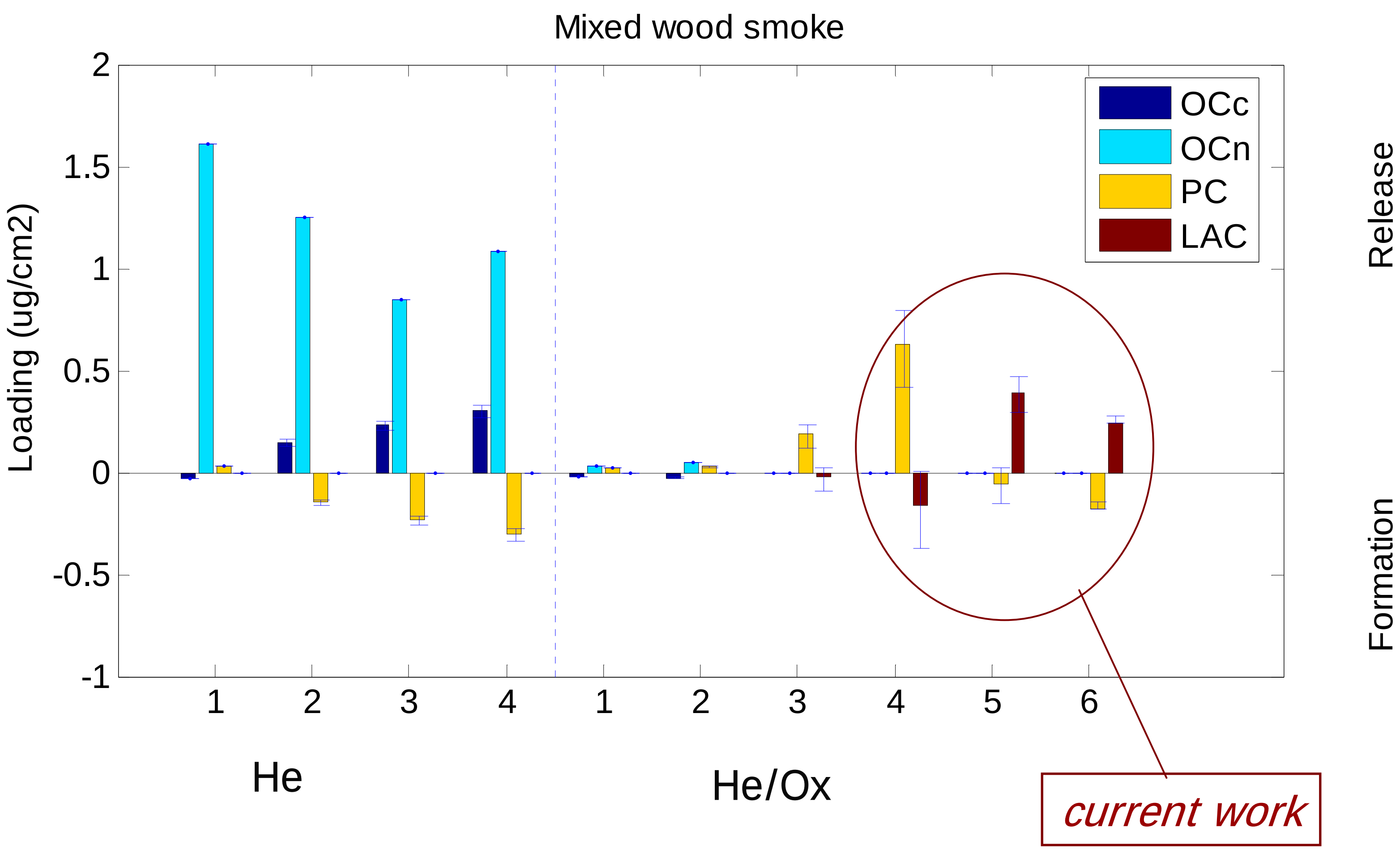
5. Back to the reactor

Reactor model results (I)



5. Back to the reactor

Reactor model results (II)



Current work: Explicit representation of assumptions

Safe assumptions

- No charring in oxygen mode

Constrainable assumptions

- PC and LAC lost in He-4 only
- Yield of OC minimal ← *currently working on representation*
- Approach: Central-min-max for each questionable assumption

Recommendations

1. Fix the laser (and give benchmarks)!
   - There's good information, but the laser is not stable enough.
2. Minimize co-evolution (650-700C)
   - Sorry, 550 <u>is not enough</u>, & we can't correct
3. Transmittance *and* reflectance
   - Transmittance sensitive to charring– may be *good*
   - Reflectance relatively insensitive to charring– may be *good*