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)

Each "artifact" can be summarized thus:

- *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)

- *Required: only 2 types of carbon evolving simultaneously.*

Formal reactor model for TOA

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

System response

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

System state

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

could have 5 (shown later)

Transfer function

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

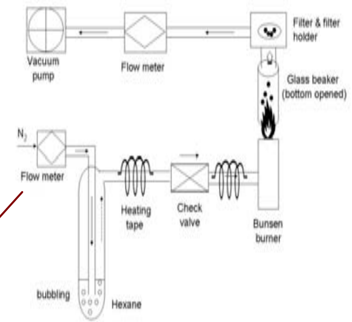
Source of the "problem"

Carbon
Optics

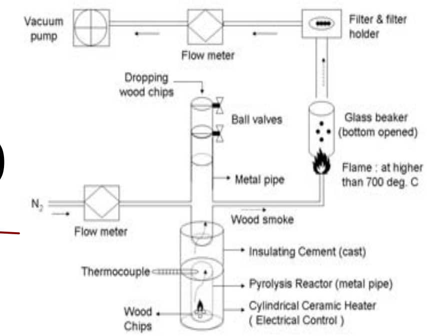
$$\begin{bmatrix} FID \\ \Delta ATN \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ K_C\sigma_C & K_N\sigma_N & K_P\sigma_P & K_L\sigma_L \end{bmatrix} \Delta \begin{bmatrix} OCc \\ OCn \\ PC \\ LAC \end{bmatrix}$$

- 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

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

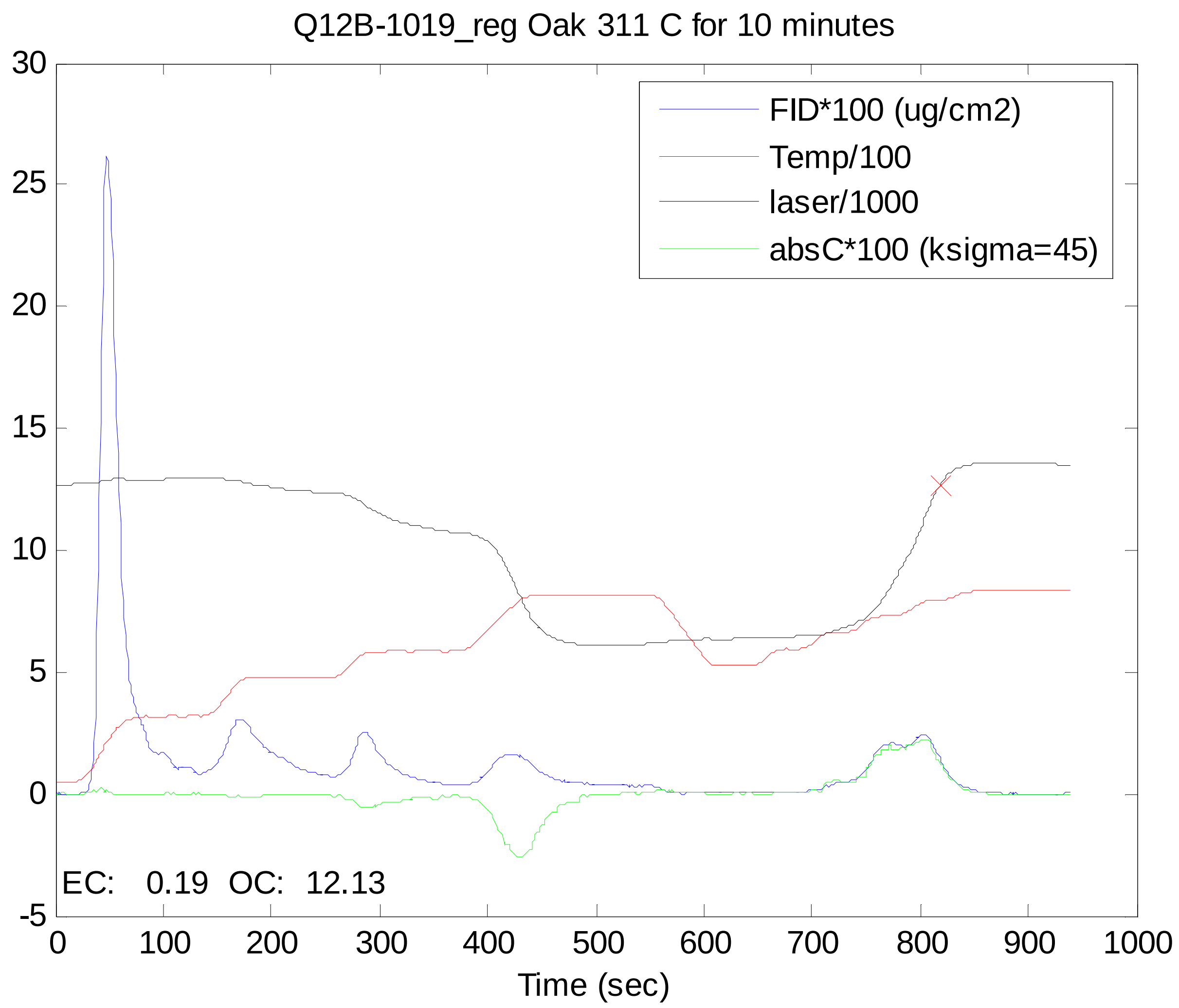
Loading of species I ($\mu g/cm^2$)

Transmittance of loaded filter

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

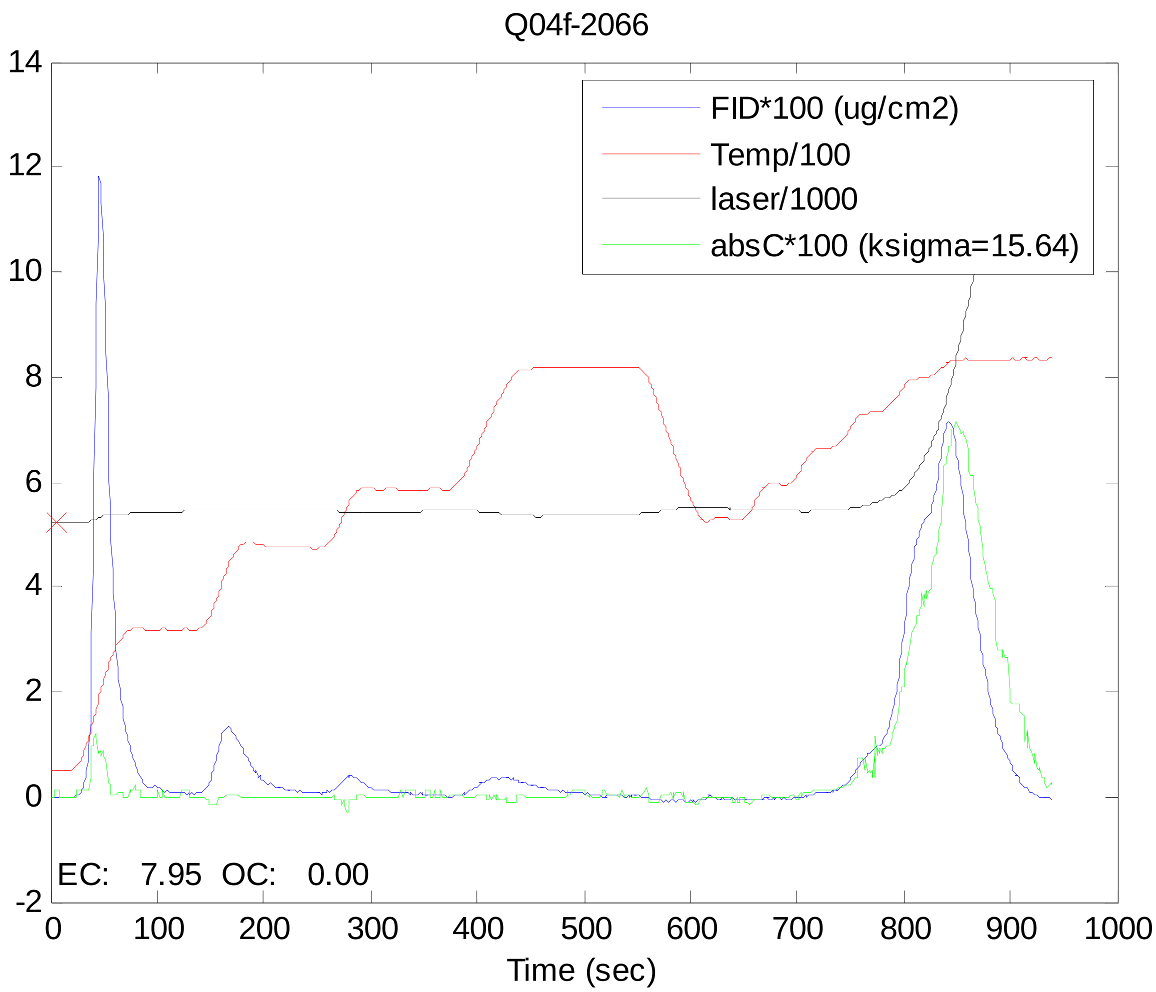
Examples to follow…

Smoldering woodsmoke “thermabsgram”



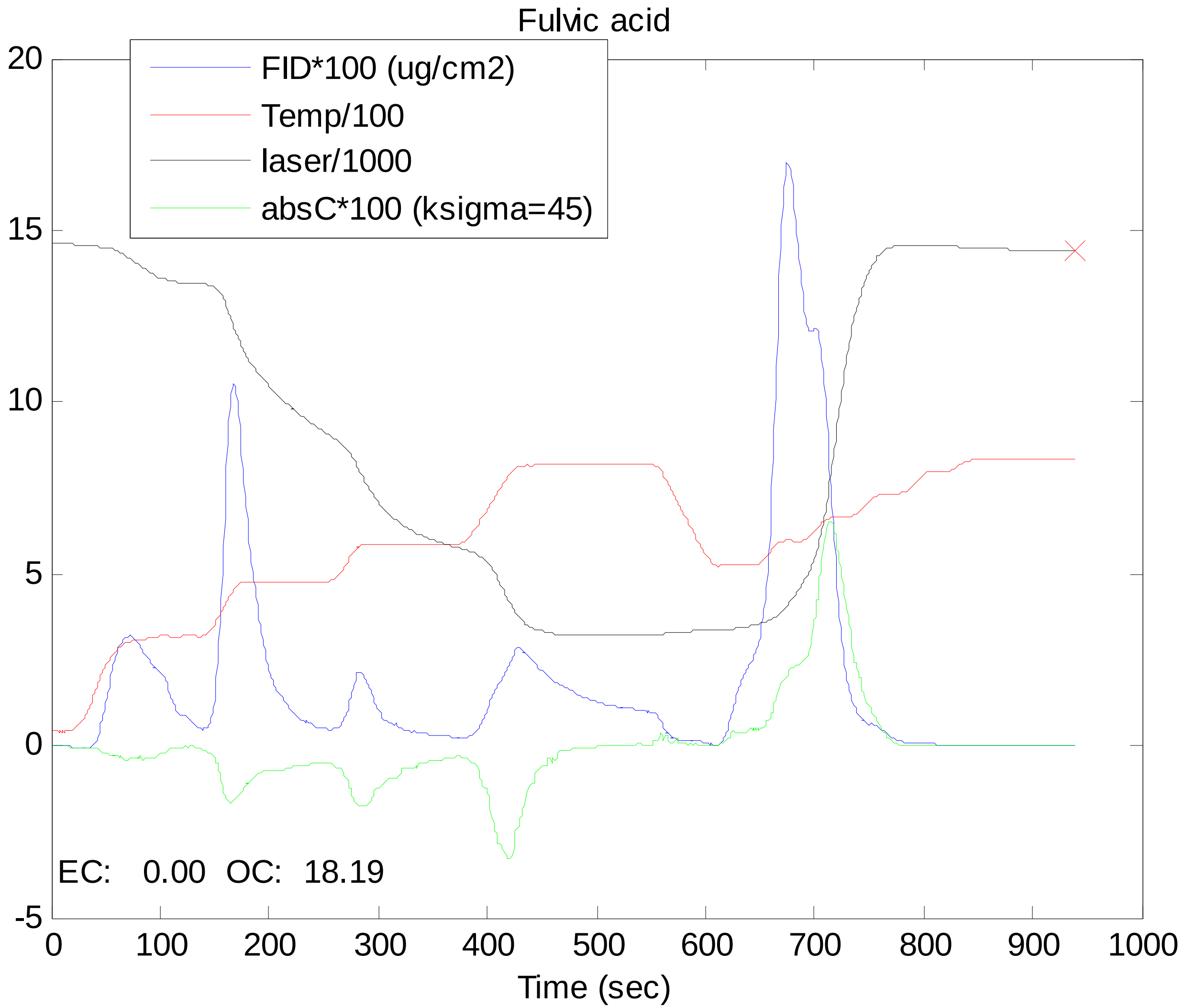
2. Optics

Diesel thermabsgram



2. Optics

Fulvic acid thermabsgram



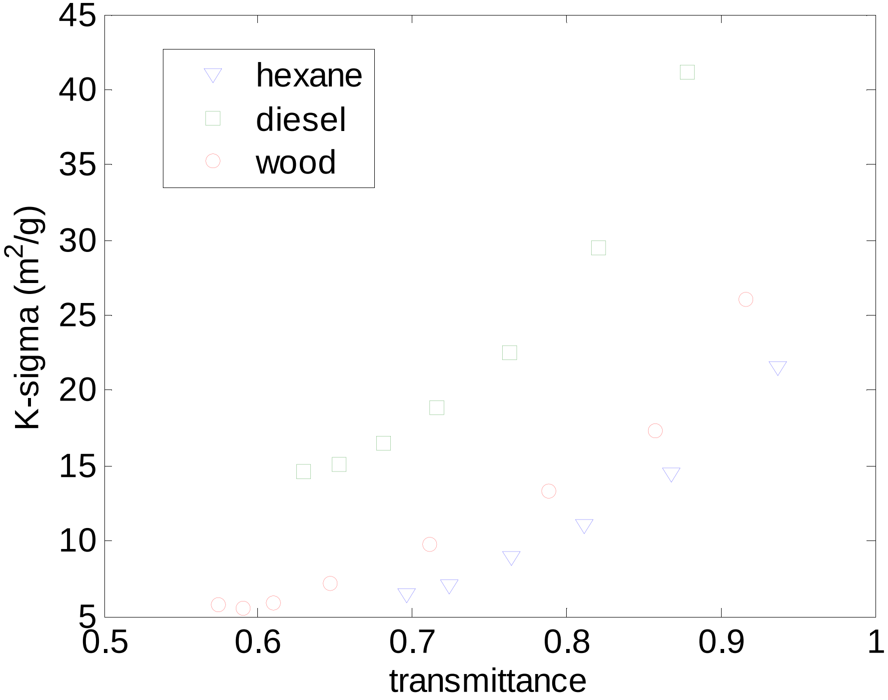
2. Optics

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:

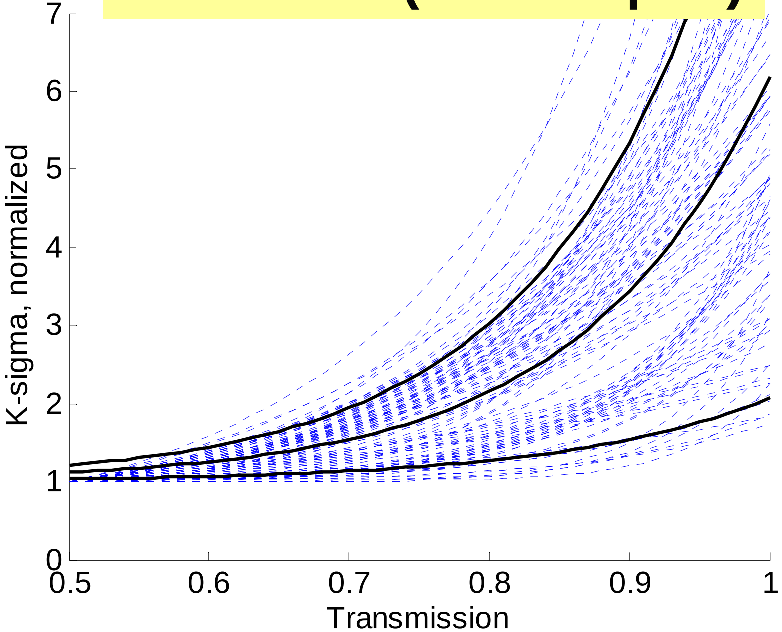
- source type
- filter transmittance
- mood



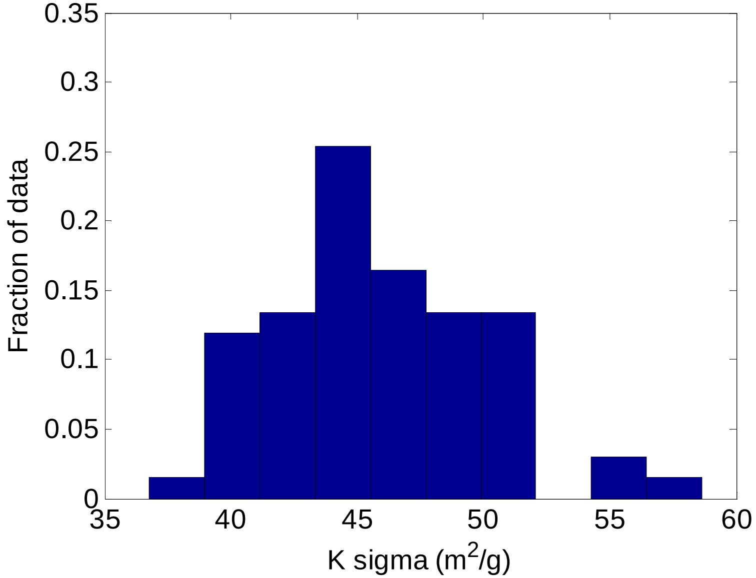
p<0.0001 (hexane-diesel-wood)

K-σ differs between native LAC & pyrolytic carbon

Native LAC (101 samples)

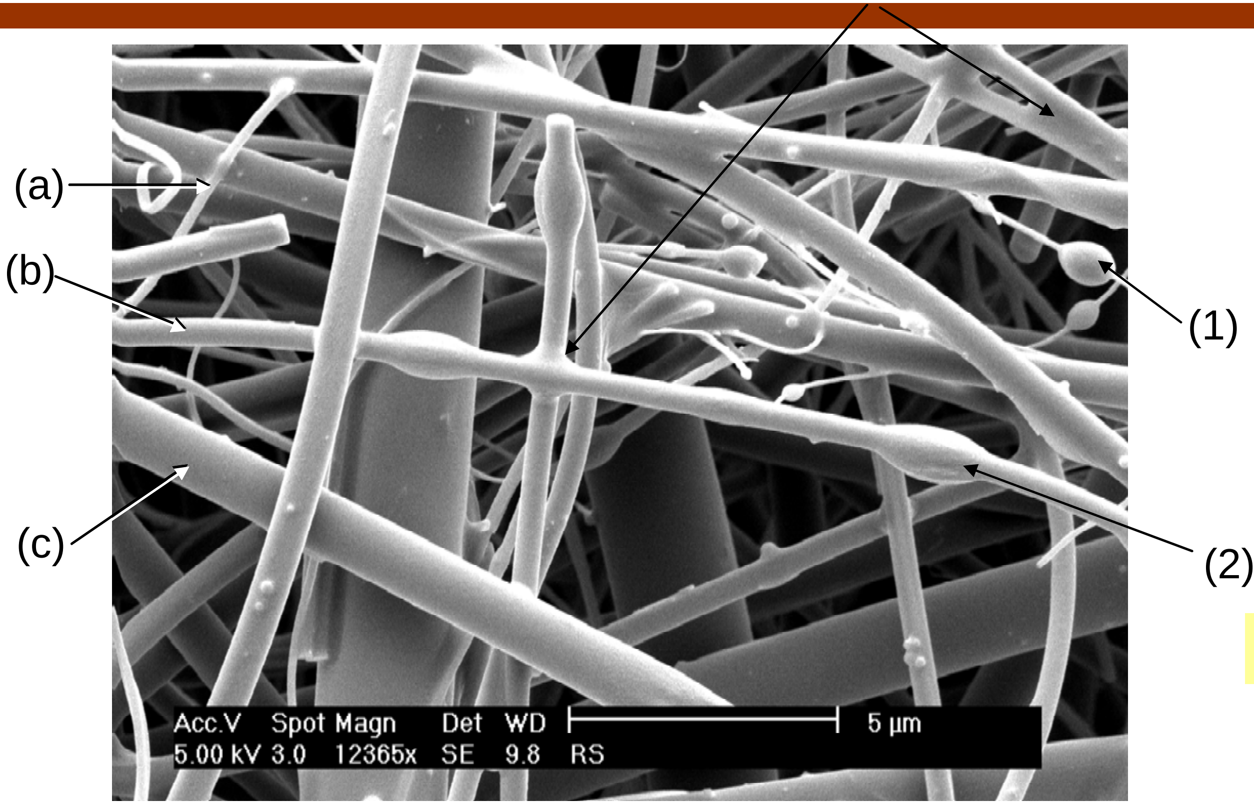


Pure pyrolytic carbon (PC)



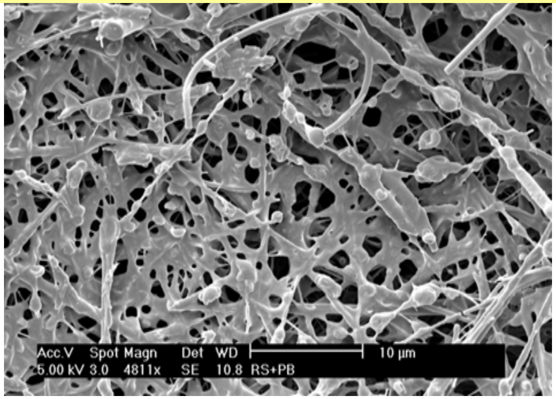
We knew that.
(Chow et al. 2004;
Subramanian et al. 2006)

Charrable carbon is liquid on filters

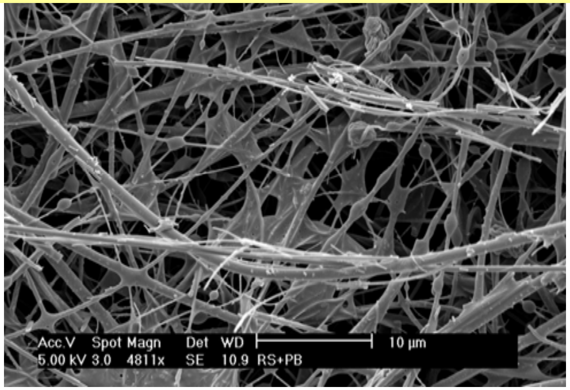


- Shapes are consistent with droplet-on-fiber theory
- Implies that most OC is present as fiber coatings

Rice straw burning (Thailand)



Wood cookstoves (Honduras)



2. Optics

Subramanian et al., 2007

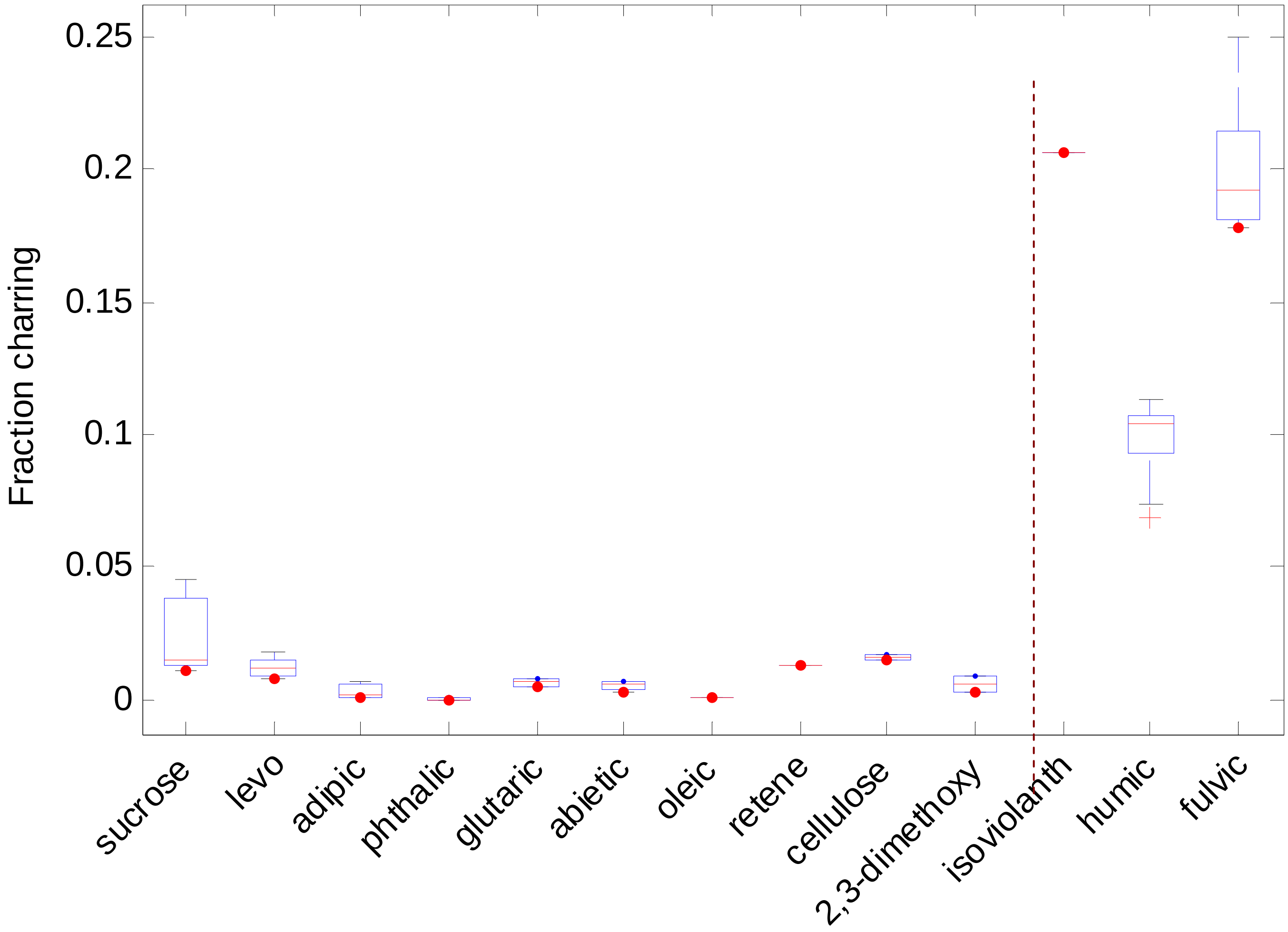
Optics summary

- 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)

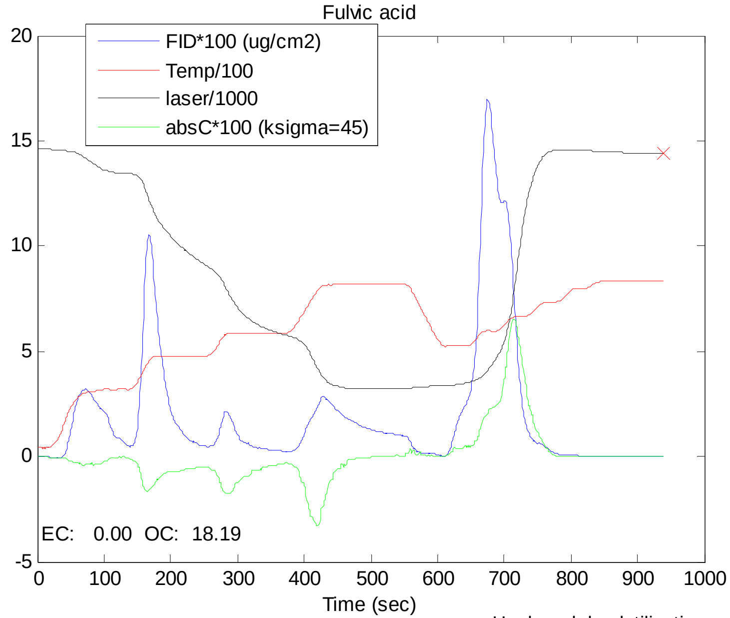
Most model compounds don't char

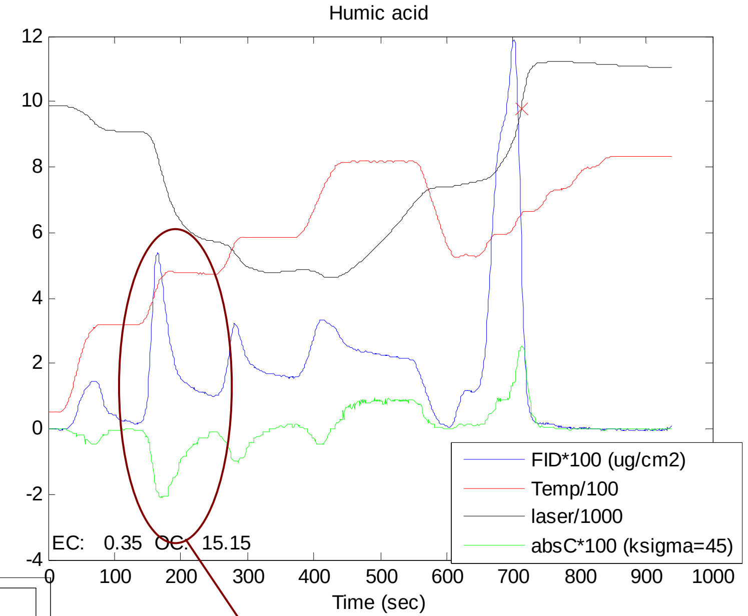


...not even water-soluble compounds!

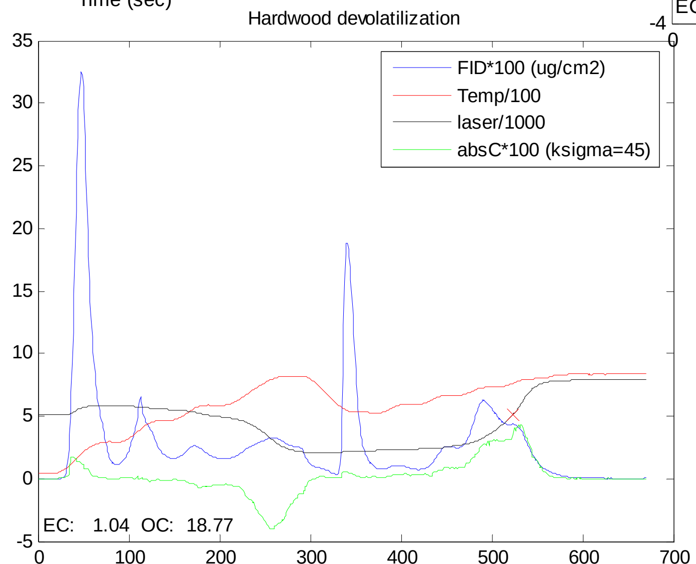
3. Charring

Complex compounds do char





"Early charring"



3. Charring

Where does "early charring" come from?

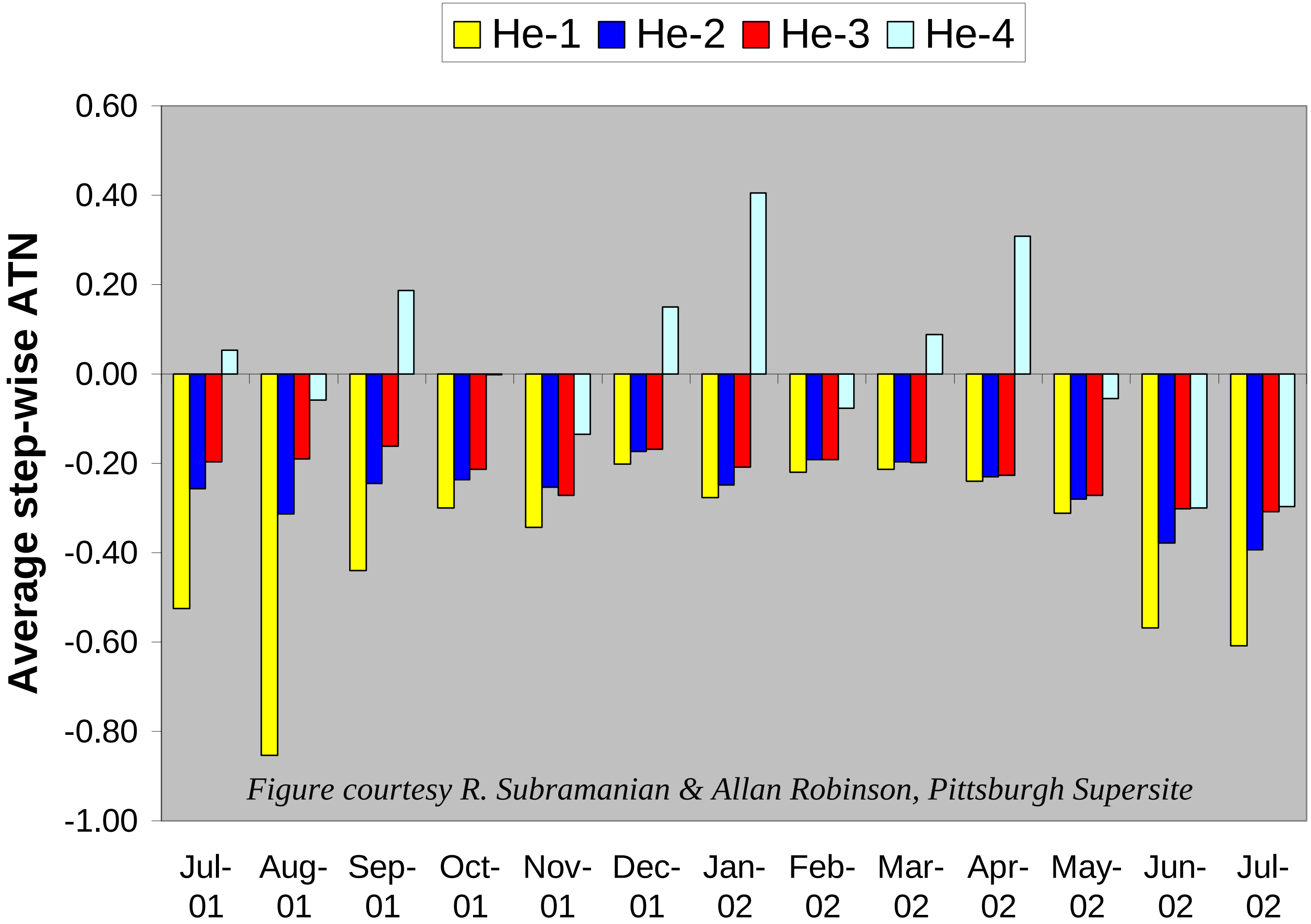
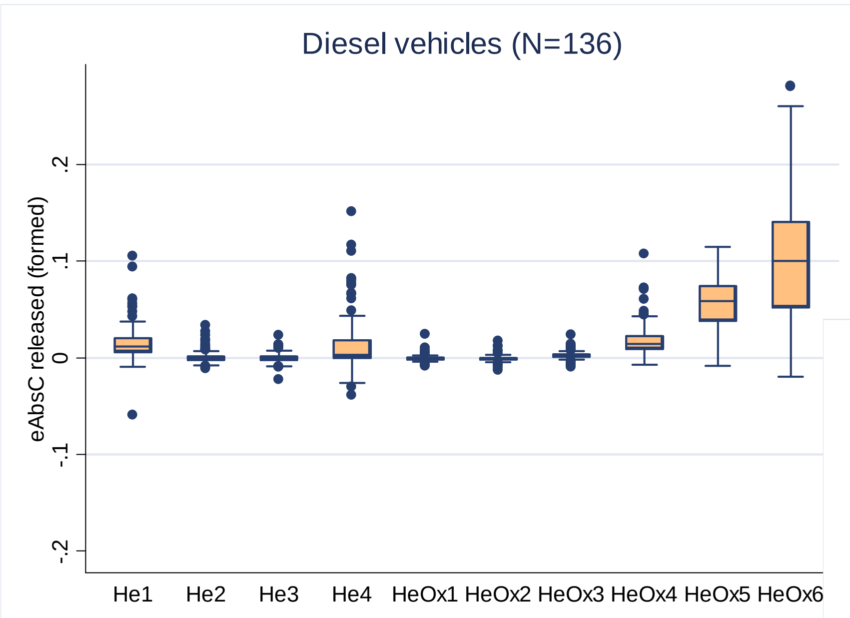
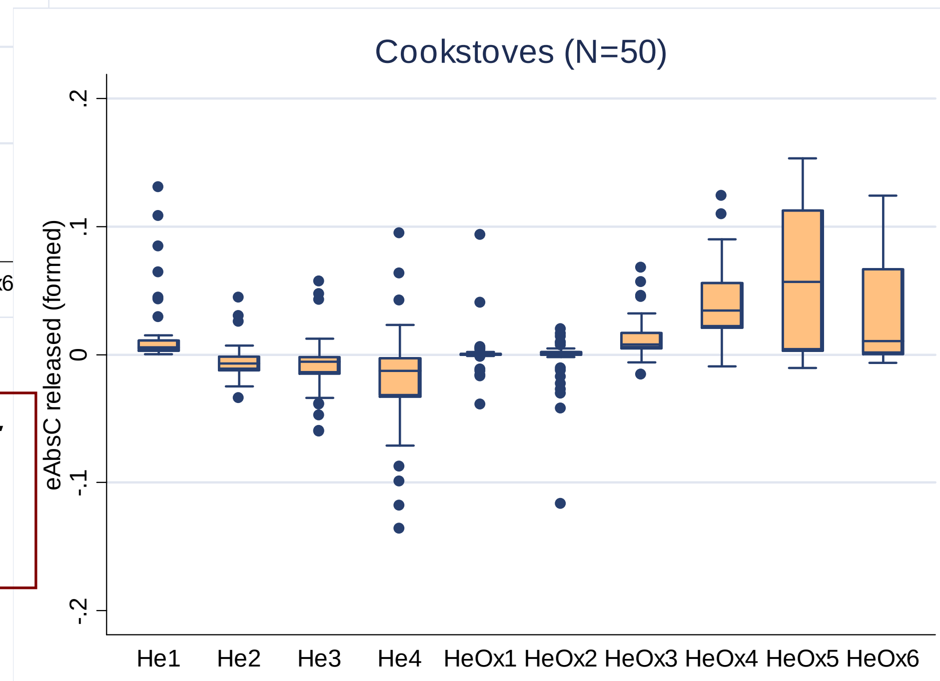


Figure courtesy R. Subramanian & Allan Robinson, Pittsburgh Supersite

3. Charring

…Not from sources!

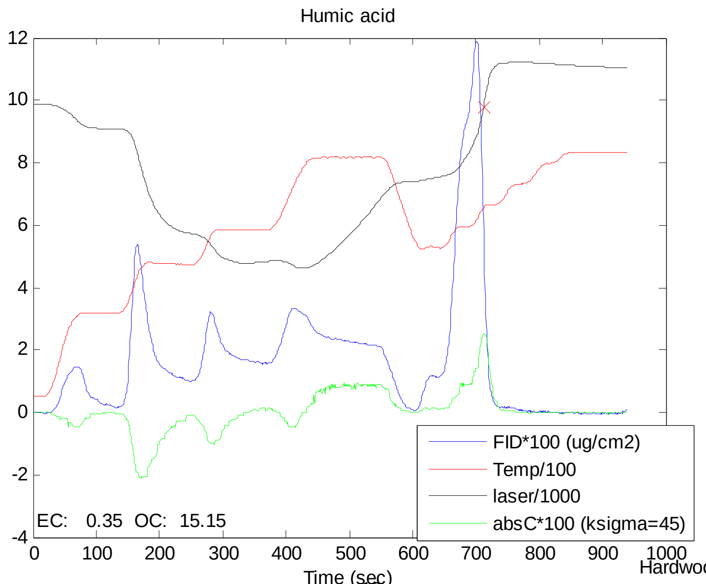


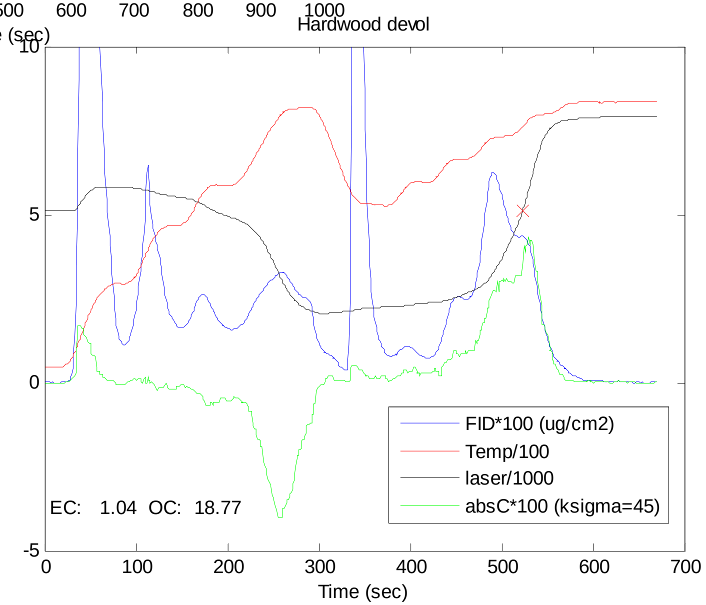


Review of pyrolysis mechanisms says: polymerized material+ catalysis→ further polymerization = charring

3. Charring

Two equations, three unknowns…





Released in He-4:

PC, LAC

(if oxygen present)

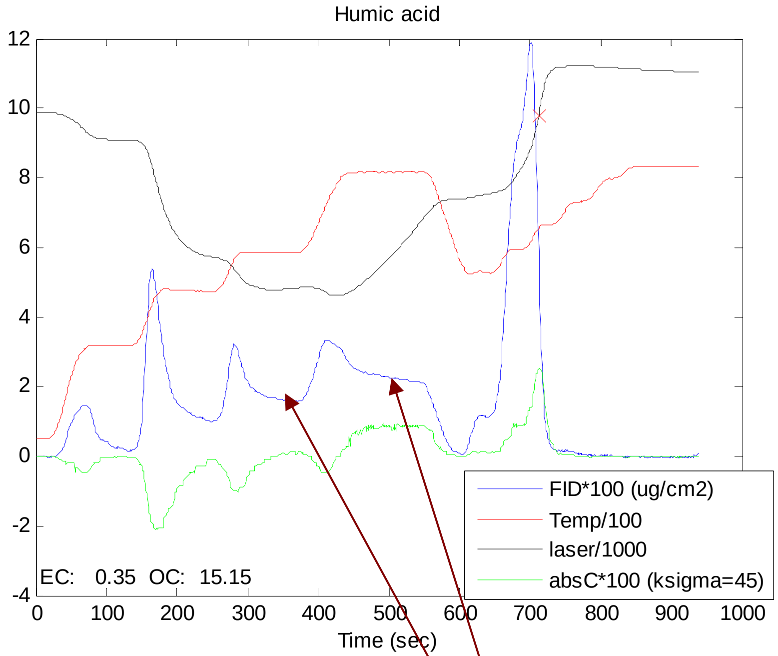
OC

Released in “early” HeOx:

OC, PC, LAC

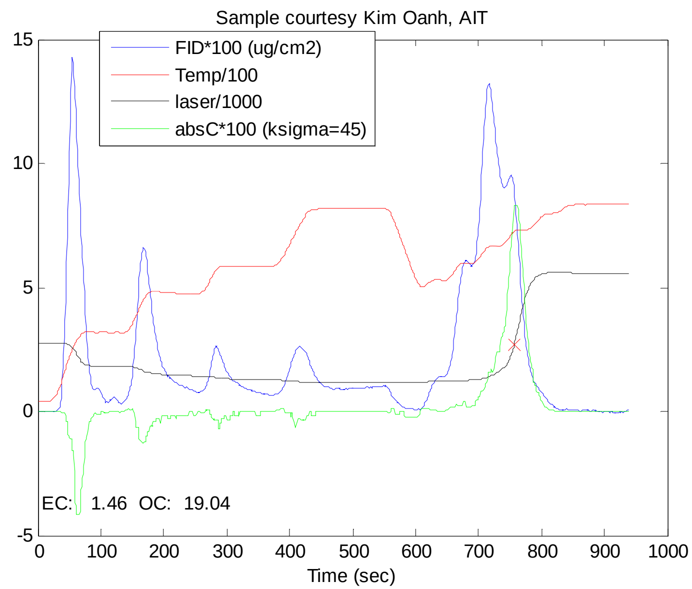
4. Kinetics?

Oh, that heavy OC…



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

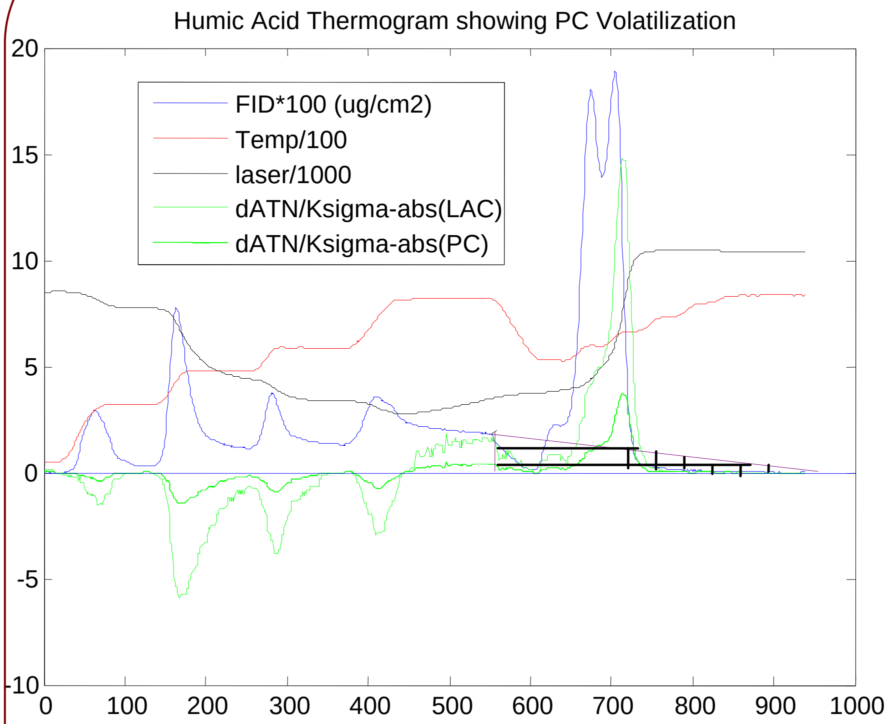
Plateau = slow volatilization

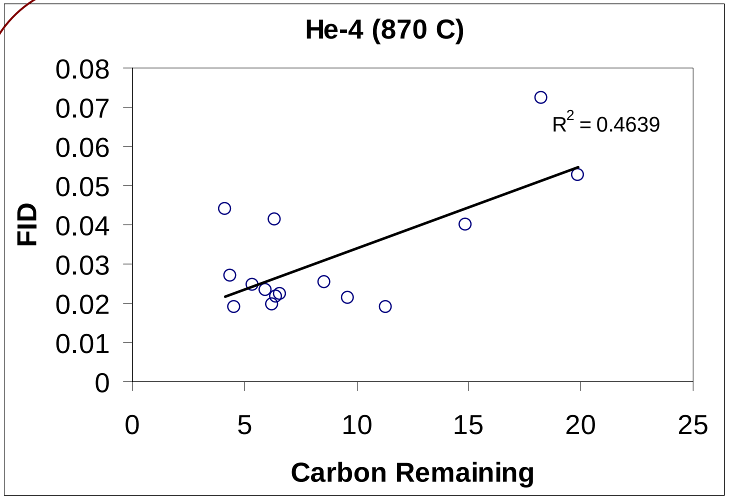


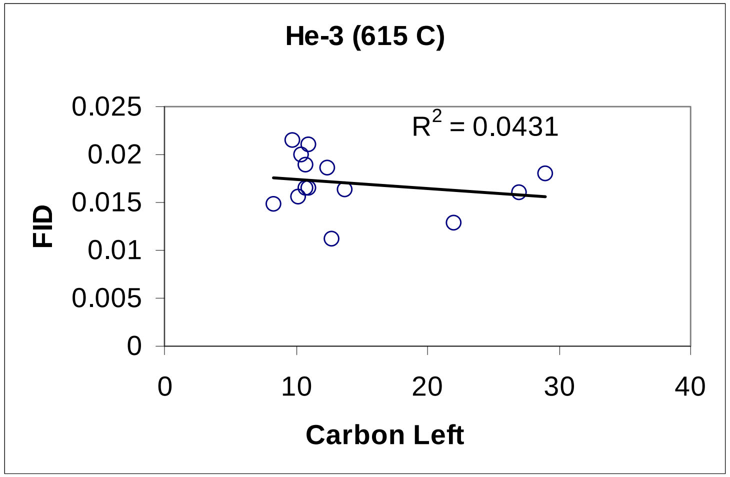
4. Kinetics?

Idea: Infer heavy OC from traces

Method 1 (Projection)







Method 2 (kinetic)

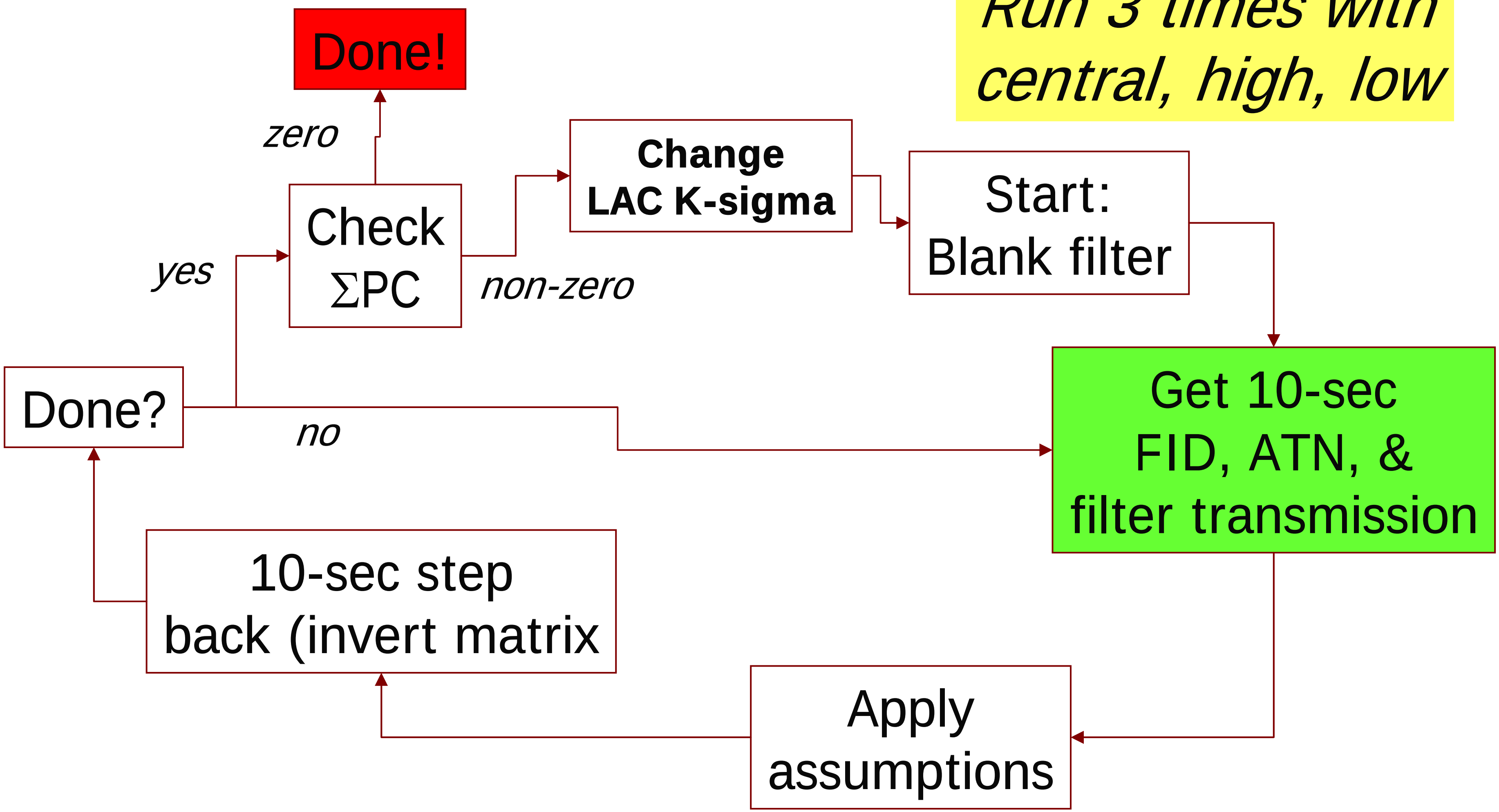
4. Kinetics?

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.

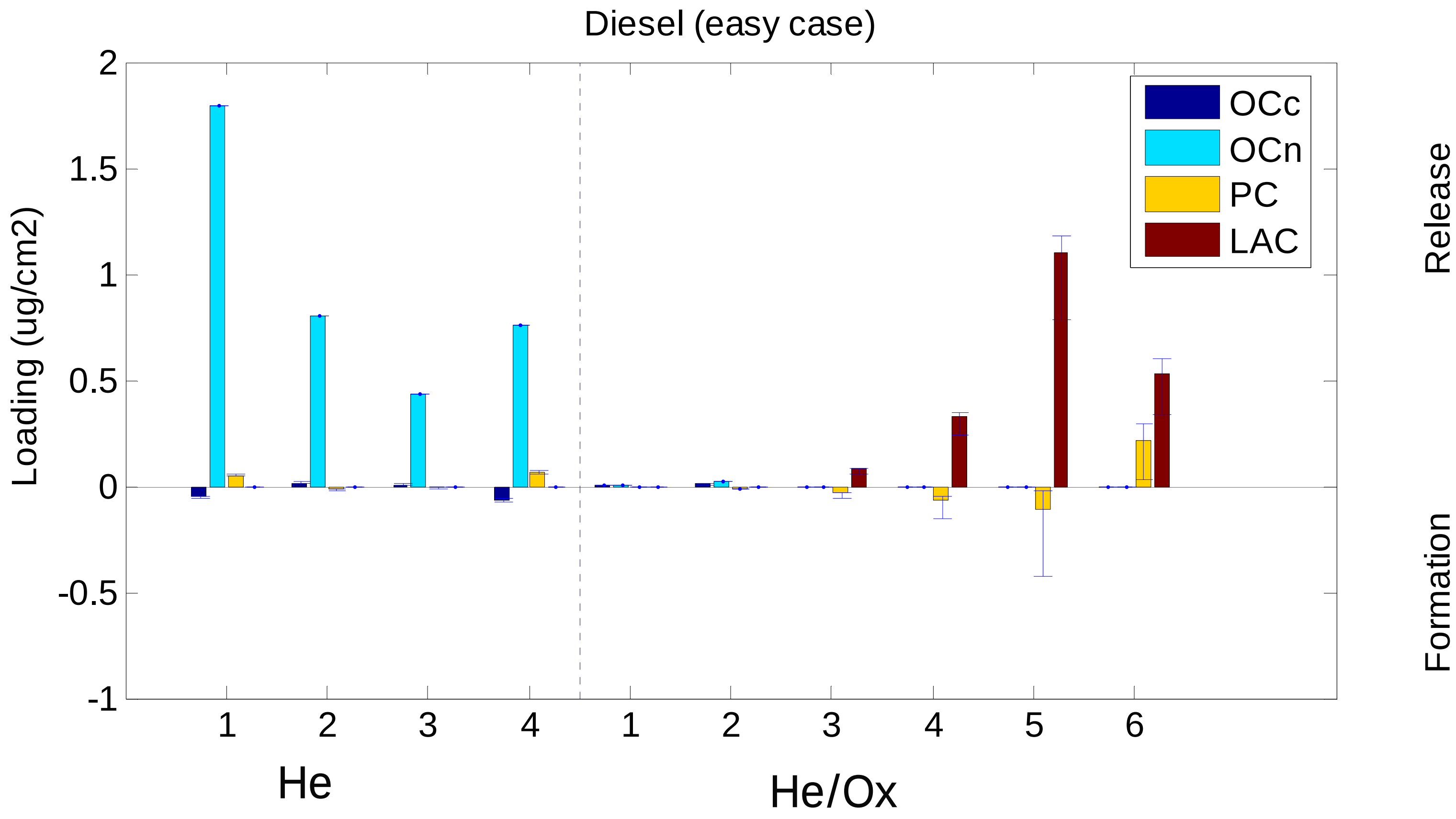
(Today's) Reactor model

Run 3 times with central, high, low



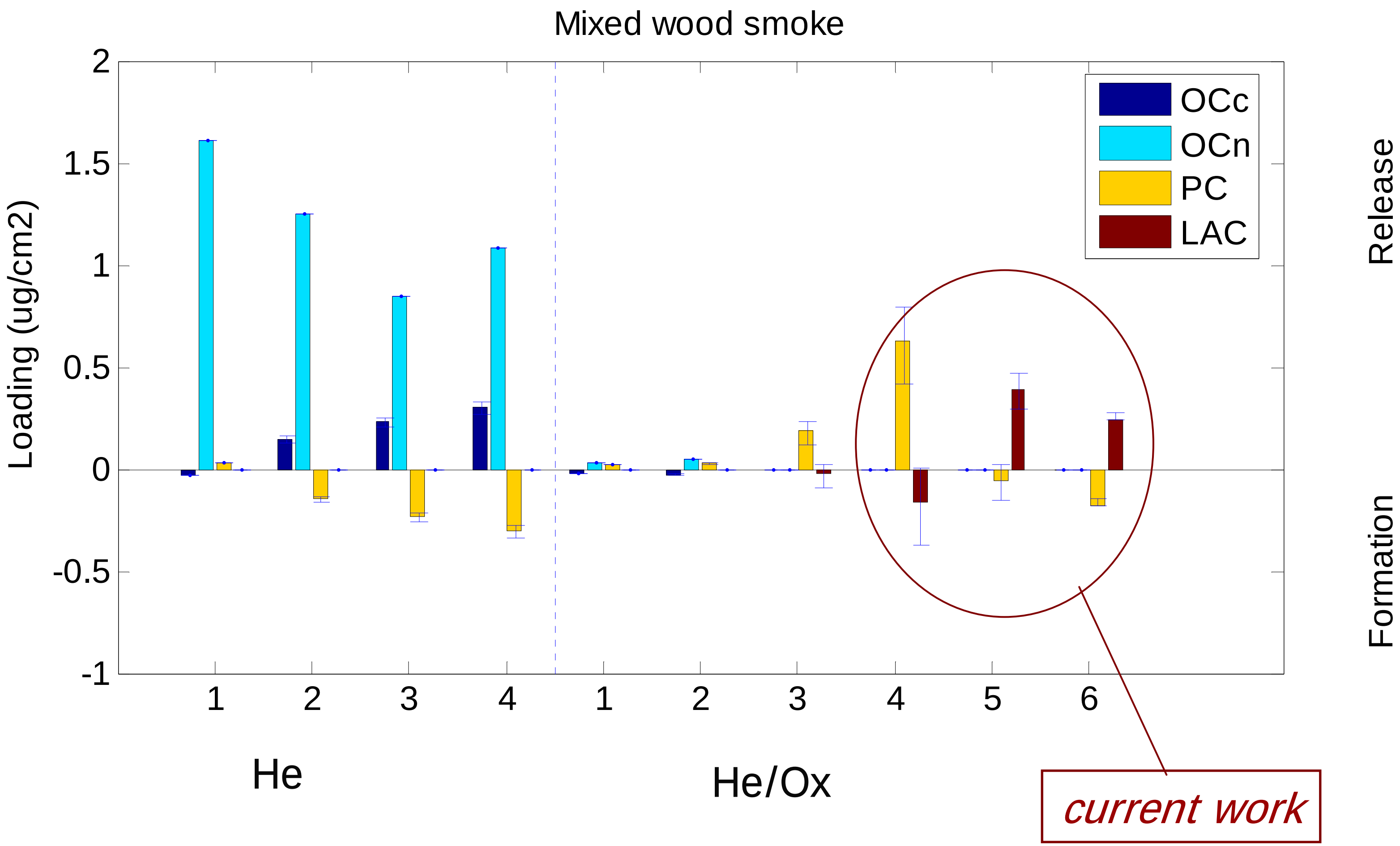
5. Back to the reactor

Reactor model results (I)



5. Back to the reactor

Reactor model results (II)



5. Back to the reactor

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*