

# Definitional Issues

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Geneva, Switzerland

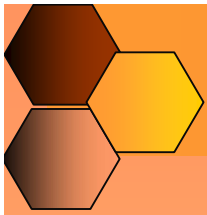
# Or, in other words...

whaaat? we don't even know what it is and you want us to add up emissions?

I mean, it *is* rather uncertain and all...

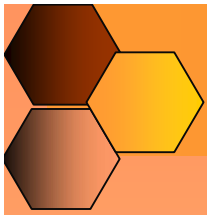


***Relax.***



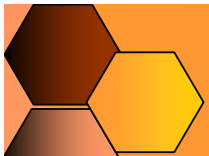
# Questions I think we are asking

- ✦ Climatic effects of carbonaceous particles depend on composition.
- ✦ There are thousands of carbon compounds.  
(obviously, we will not model each individually)
- ✦ What **divisions between carbon types** *must* we draw to represent effects on climate?
- ✦ Can we measure those divisions **in practice?**

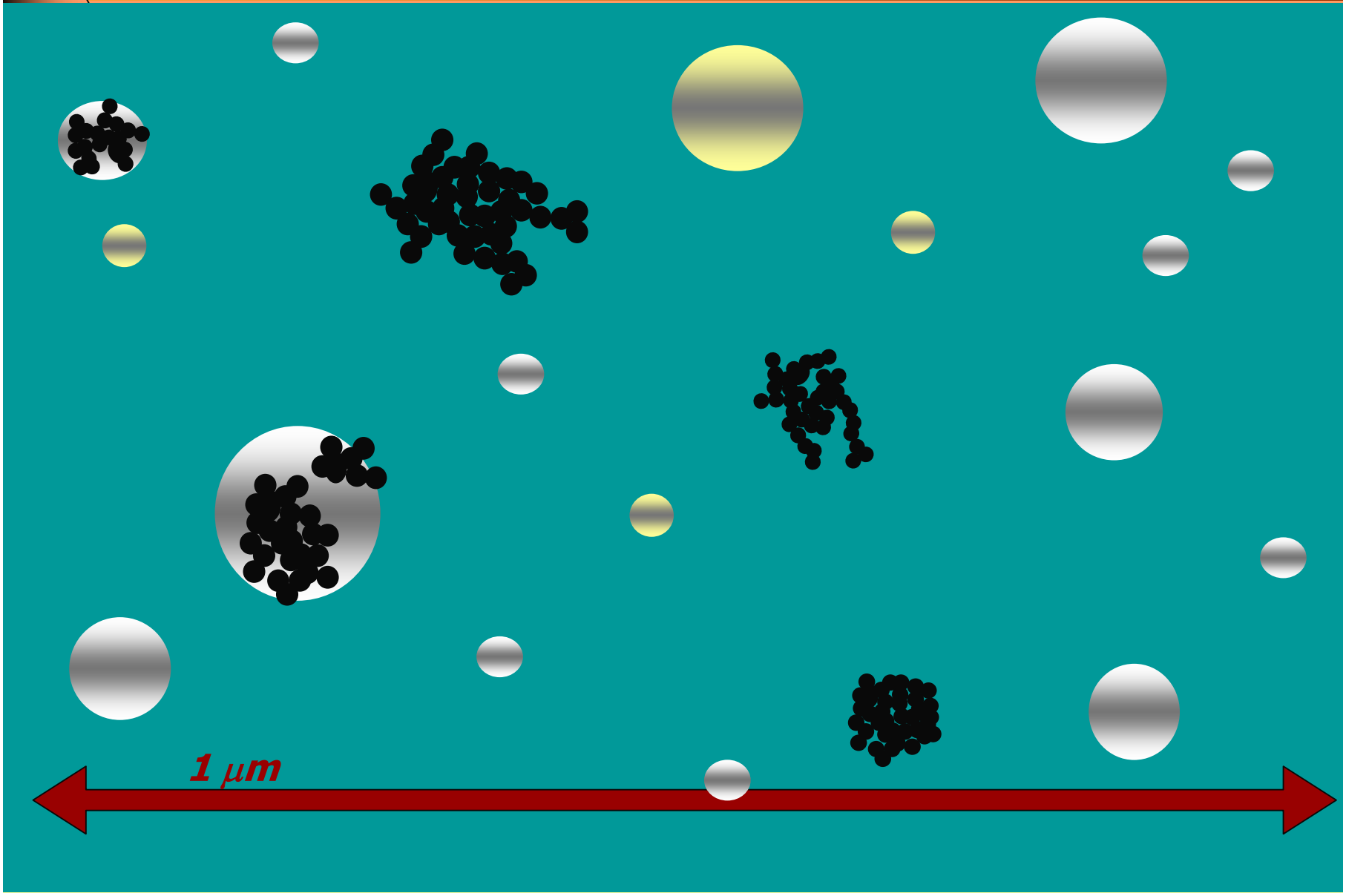


# What I'll cover here

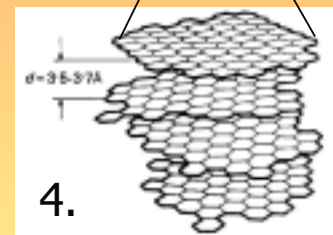
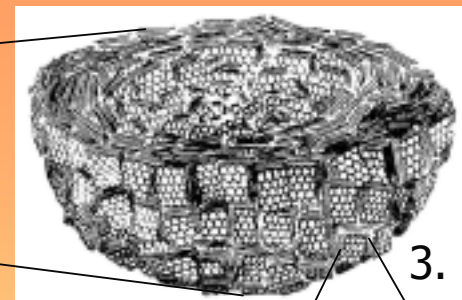
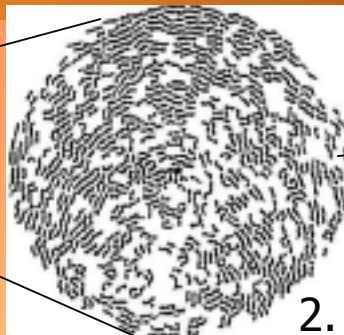
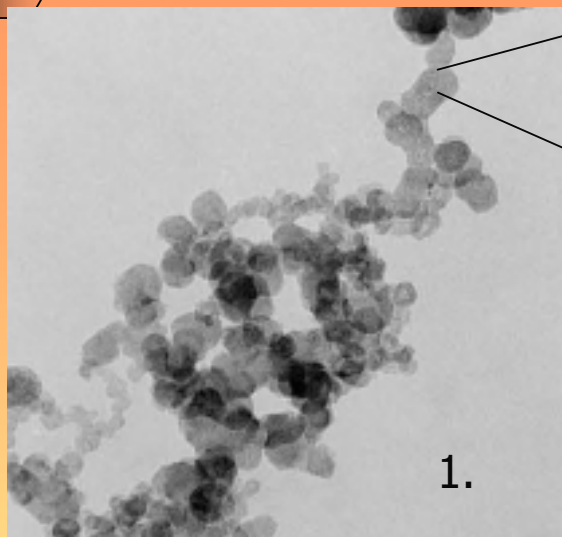
1. carbon particles... hmm.
  - a. could you identify a black carbon particle  
...if you had nanovision?
  - b. Houston, we have a (measurement) problem
  - c. what can we do with all these names?
2. modeled climate forcing
  - a. overview: forcing calculations
  - b. the pieces: direct forcing
  - c. some comments: indirect forcing
3. summary: role of definitions



# If you had microvision...



# Nanovision (and a very small scalpel)



1. *Micrograph of diesel soot*: Stanmore, Brillhac, and Gilot, *Carbon* **2001**, 39, 2247-2268.
2. *Structure of spherule extracted from HRTEM image*: Palotás et al., *Energy and Fuels* **1996**, 10, 254-259.
- 3, 4. *Structure of spherule and layers inferred from electron microscopy and X-ray diffraction*: Heidenreich, Hess and Ban, *J. Appl. Crystallography* **1968**, 1, 1-19

Structure has been known for many years.

Heckman, F.A. Microstructure of carbon black.

*Rubber Chem. Technol.* **1964**, 37, 1245-1298.

# Nanovision (and a very good chemistry set)

*thousands of compounds  
much carbon and hydrogen  
sometimes oxygen &  
a little nitrogen*

Schauer, J.J.; Kleeman, M.J.; Cass, G.R.; Simoneit, B.R.T., *Environ. Sci. Tech.* **1999**, *33*, 1578-1587.

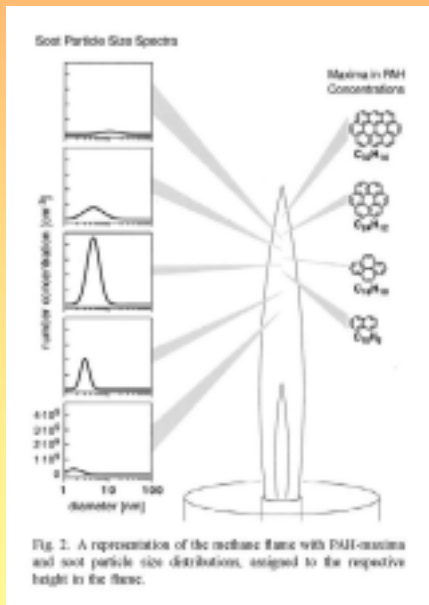
TABLE 2. Organic Compounds Present in Diesel Fuel and in Medium Duty Diesel Truck Exhaust

compound	diesel-powered medium duty truck emissions (µg km <sup>-1</sup> )		diesel fuel composition (µg g <sup>-1</sup> )	ref. 1	compound	diesel-powered medium duty truck emissions (µg km <sup>-1</sup> )		diesel fuel composition (µg g <sup>-1</sup> )	ref. 1
	gas phase	particle phase				gas phase	particle phase		
n-hexane	2810		A	A	n-octadecane	681	2.04	6212	A, F
n-heptane	1800		A	A	n-nonadecane	611	3.62	1828	A, F
n-octane	410		A	A	n-tricosane	280	65.7	1630	A, F
n-nonane	260		A	A	n-tetracosane	65.2	42.5	5278	A, F
n-decane	300		A	A	n-pentacosane	52.0	83.8	412	A, F
n-undecane	4		A	A	n-hexacosane	45.5	2018	10	A, F
n-dodecane	500		10000	A, F	n-heptacosane	43.1	1480	4	A, F
n-tridecane	417		10700	A, F	n-octacosane	28.1	758	10	A, F
n-tetradecane	629		13300	A, F	n-nonacosane	34.0	290	10	A, F
n-pentadecane	368	2.12	10600	A, F	n-triacontane	25.1	308	10	A, F
n-hexadecane	213	5.62	10700	A, F	n-tritriacontane	19.1	16	10	A, F
n-heptadecane	614	5.92	5700	A, F	n-tetracontane	6.1			A, F
isopentane	2340		A	A	2,4-dimethylhexane	50			A, A, A
2,2-dimethylbutane	310		A	A	2,3,4-trimethylpentane	390			A, A, A
2,3-dimethylbutane	510		A	A	2,3-dimethylhexane	160			A, A, A
2-methylpentane	830		A	A	2-methylheptane	180			A, A, A
3-methylpentane	810		A	A	3-methylhexane	270			A, A, A
2,4-dimethylpentane	410		A	A	isoheptane	380		10200	A, F
2-methylhexane	510		A	A	heptane	434	4.1	6228	A, F
2,3-dimethylpentane	570		A	A	2,6,10-trimethylheptadecane	36.1	5.2	1838	A, F
3-methylhexane	310		A	A	octadecane	540	4.0	2618	A, F
2,2,4-trimethylpentane	1240		A	A	pristane	443		5840	A, F
2,5-dimethylhexane	50		A	A	phytane	400		5718	A, F
isobutane	3560		A	A	n-butane	50			A, A, A
isopentane	360		A	A	1,4-cyclohexane	140			A, A, A
1,2-dimethylcyclohexane	520		A	A	cis-2-hexene	180			A, A, A
cis-2-pentene	260		A	A	trans-2-hexene	180			A, A, A
trans-2-butene	1340		A	A	cis-2-heptene				A, A, A
3-methyl-1-butene	360		A	A					A, A, A
2-methyl-1-butene	260		A	A	2-methyl-2-pentene	290			A, A, A
1,3-butadiene	310		A	A					A, A, A
ethylene	4400		A	A					A, A, A
cyclopentane	410		A	A					A, A, A
1-methylcyclopentane	620		A	A					A, A, A
cyclohexane	210		A	A					A, A, A
1-methylcyclohexane	520		A	A					A, A, A
1,2-dimethylcyclohexane	830		A	A					A, A, A
1,3-dimethylcyclohexane	140		A	A					A, A, A
1,4-dimethylcyclohexane	280		A	A					A, A, A
1,2,4-trimethylcyclohexane	28.2		A	A					A, A, A
1,3,5-trimethylcyclohexane	24.1		A	A					A, A, A
1,2,4,5-tetramethylcyclohexane	38.2		A	A					A, A, A
cycloheptane	210		A	A					A, A, A
benzene	2340		A	A					A, A, A
toluene	1800		A	A					A, A, A
o-xylene	410		A	A					A, A, A
m-xylene	2330		A	A					A, A, A
p-xylene	830		A	A					A, A, A
1,2,4-trimethylbenzene	300		A	A					A, A, A
1,3,5-trimethylbenzene	520		A	A					A, A, A
1,2,4,5-tetramethylbenzene	210		A	A					A, A, A
1,2,4,6-tetramethylbenzene	260		A	A					A, A, A
naphthalene	860		A	A					A, A, A
2-methylnaphthalene	617		500	A, F					A, A, A
1-methylnaphthalene	817		860	A, F					A, A, A
1-methylanthracene	370		580	A, F					A, A, A
1,2,3-trimethylbenzene	542		2050	A, F					A, A, A
1,2,4-trimethylbenzene	240		1300	A, F					A, A, A
1,2,5-trimethylbenzene	93.0	180	700	A, F					A, A, A
1,2,6-trimethylbenzene	18.1			A, F					A, A, A
1,3,5-trimethylbenzene	18.3			A, F					A, A, A
1,2,3,4-tetramethylbenzene	24.6	6.5	52	A, F					A, A, A

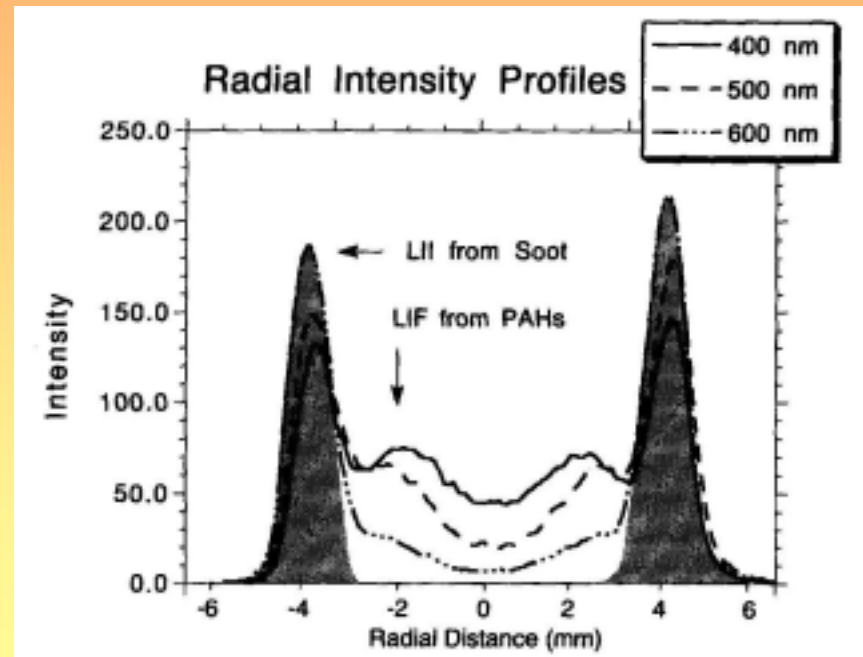
TABLE 2. ORGANIC COMPOUNDS PRESENT IN DIESEL FUEL AND IN MEDIUM DUTY DIESEL TRUCK EXHAUST

# Information from combustion research

- "soot" appears to form in a very narrow region (now you don't see it, now you do)
- implies there is a sharp difference between "special" BC and other
- caveat: most formation studies look only at simplified situations; is this true for real combustion?



Siegmann, K.; Sattler, K.; Siegmann, H.C. *J. Electron Spectrosc. Rel. Phenom.* **2002**, *126*, 191-202.



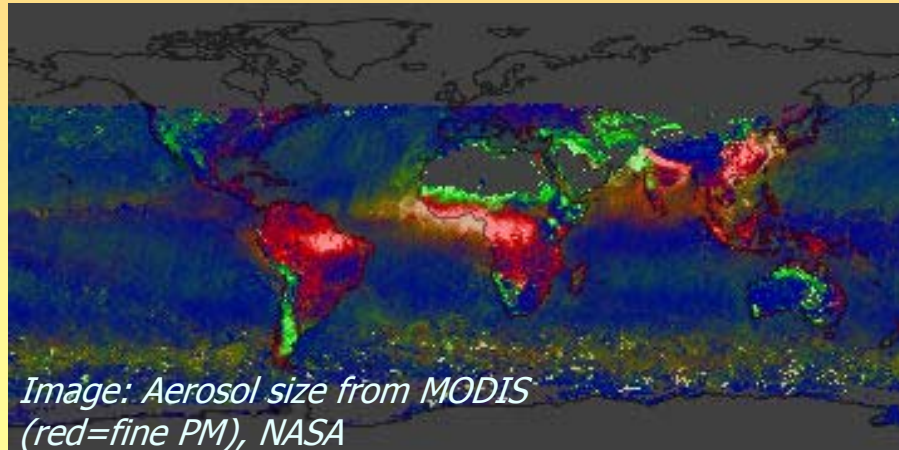
Van der Wal, R.L.; Jensen, K.A.; Choi, M.Y. *Comb. Flame.* **1997**, *109*, 399-414.

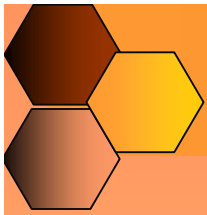


# Measurement goals (I)

We can't measure climate forcing by individual constituents.

- ✦ Aerosol concentrations are patchy  
Individual measurements don't represent the globe.
- ✦ Satellites can measure globally  
but they can't distinguish components, nor tell the difference between anthropogenic and natural.





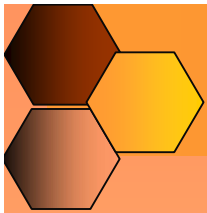
## Measurement goals (II)

Thus, we have to model the forcing. Measurements can:

- ✦ Provide model inputs
- ✦ Corroborate model results

For this purpose, the measurements must:

- ✦ Distinguish between important groups of carbon compounds
- ✦ Measure a *conserved* property



# measurement tools

- ✦ combustion analysis → total carbon
- ✦ light absorption → dark carbon
- ✦ thermal-optical analysis  
→ some carbon division (light/dark?)
- ✦ gas chromatography/mass spectrometry  
→ individual species
- ✦ Fourier Transform Infrared  
→ functional groups
- ✦ soluble fraction
- ✦ single-particle analysis

OK \*

next

next

identifies 10-20% of carbon

useful but expensive

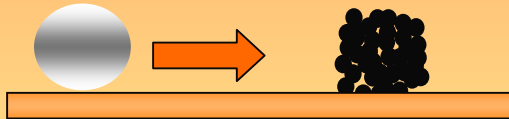
real-time ability is new

useful but expensive

\* *not immune to measurement artifacts, though*

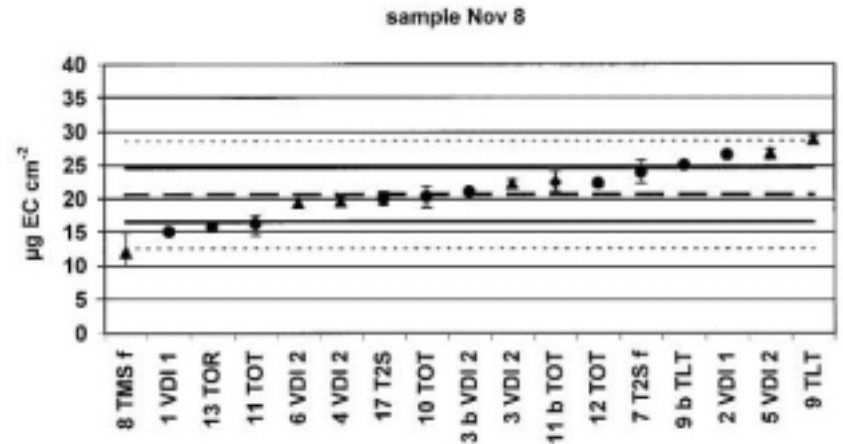
# measurements: thermal

- ✦ Principle: Heat, measure carbon released at different temperatures
- ✦ Complication 1: Charring during analysis



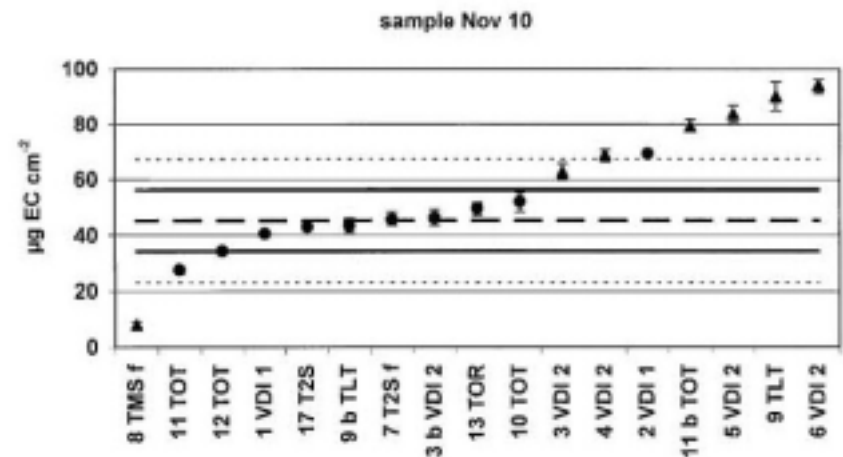
- ✦ Complication 2: Oxidation rates can vary in different mixtures
- ✦ Different protocols (rates/magnitudes of heating) yield different results

*Interlab comparison of same filter*



(b)

Lab# / method

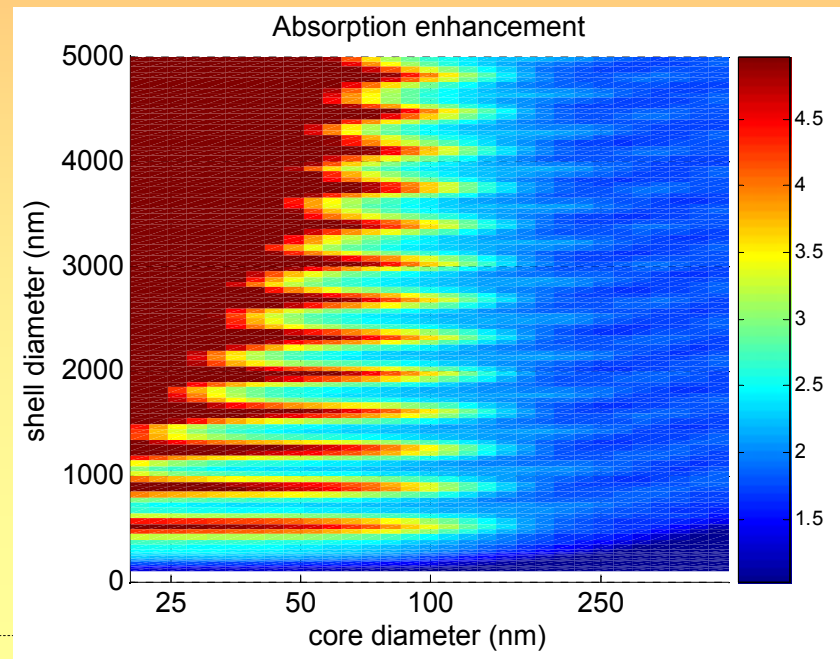
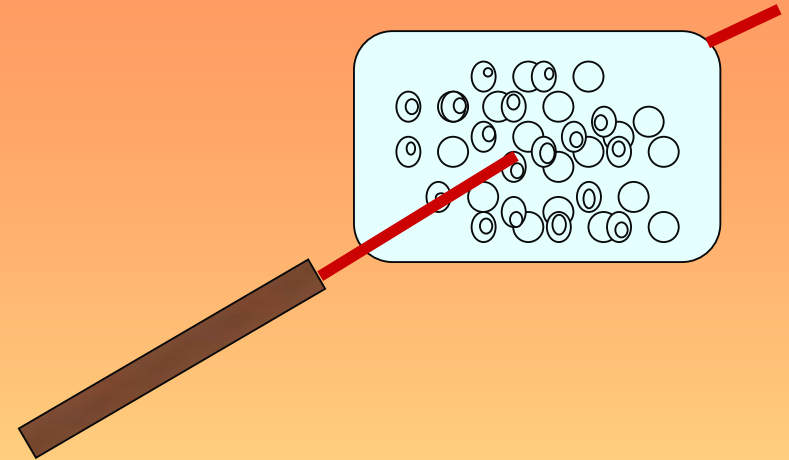


(c)

Lab# / method

# measurements: optical

- ✦ Principle: Collect particles on filter; monitor transmittance
- ✦ Complication 1: Amplification by filter (x2-4)
- ✦ Complication 2: Absorption per mass changes with particle form
- ✦ Complication 3: Non-carbon absorbers (dust?)
- ✦ Drawback: Doesn't measure negligibly-absorbing particles
- ✦ Different protocols (filters, wavelengths) and locations yield different results



# All those names!

*graphitic carbon*

"substance that almost looks like graphite"  
"result of Raman spectroscopy"

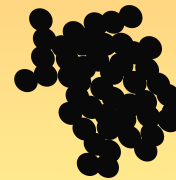
By the way,  
there's little enough  
information that we use  
*any* of these to inform  
models.

*elemental carbon*

"substance we talk about for air quality"  
"result of thermal measurement"

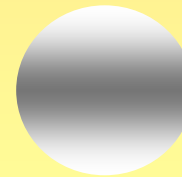
*black carbon*

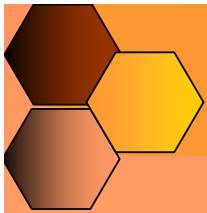
"substance used in climate models"  
"result of optical measurement"



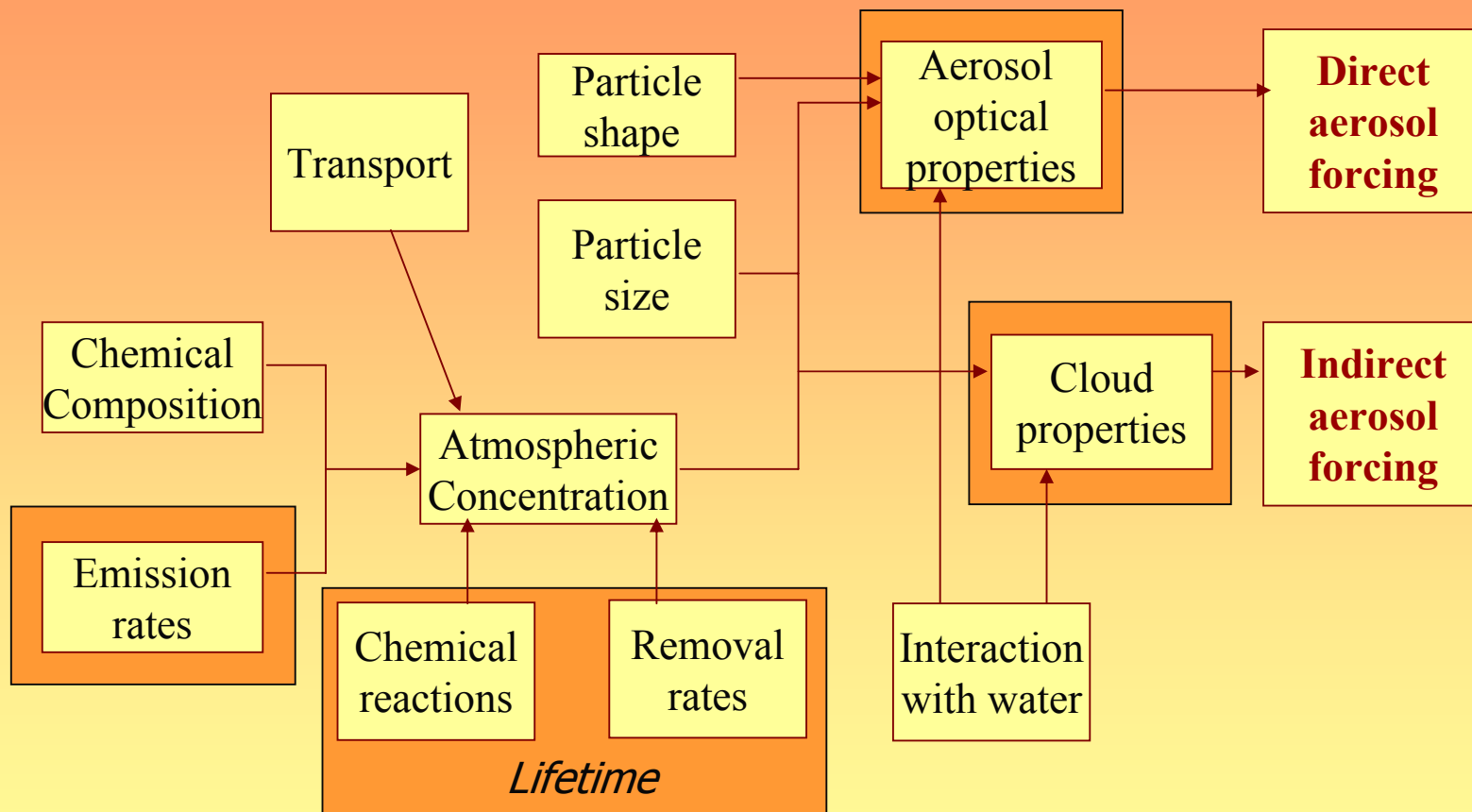
*organic carbon*

"everything else"





# Modeling procedure



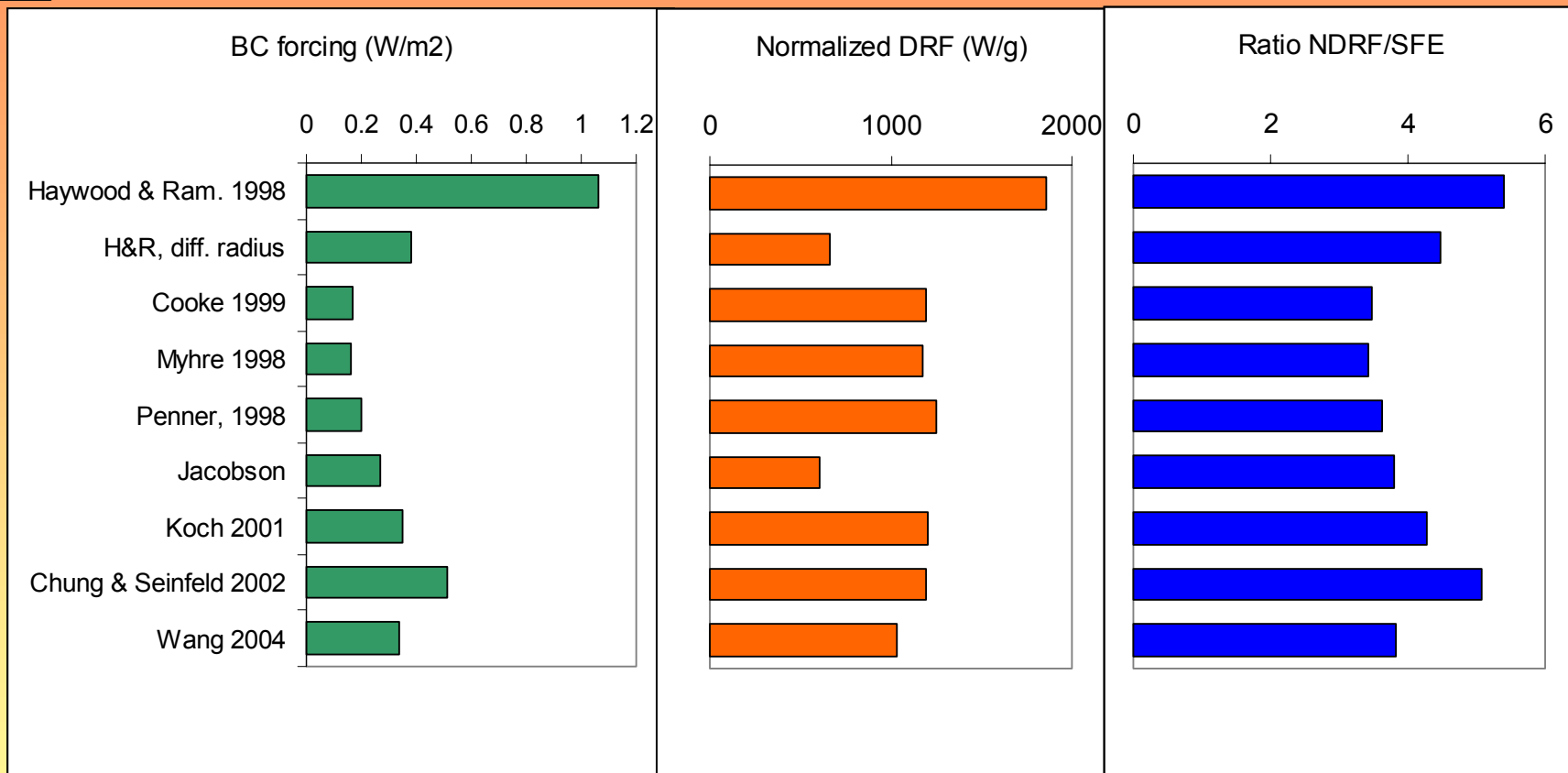


# Aerosol lifetime estimates

- ✦ Few ways to measure; must be modeled
  - Depends on meteorology (esp. rainfall)
  - Estimates are about  $\sim 1$  week
- ✦ Model corroborated by comparison with measurements
- ✦ Hard to make that comparison unless quantity measured is invariant!



# Model comparisons: black carbon



coef. var: 73% (unfair)

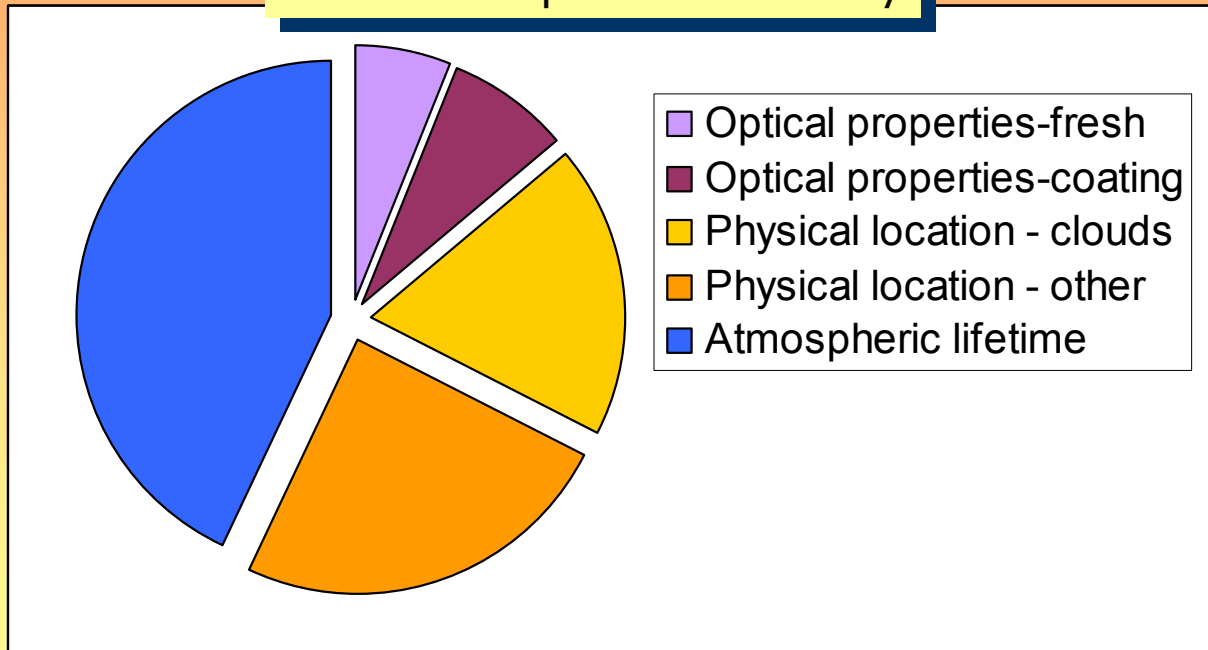
accounting for emission  
& lifetime differences  
coef. var: 32%

accounting for optical  
property differences  
coef. var: 17%

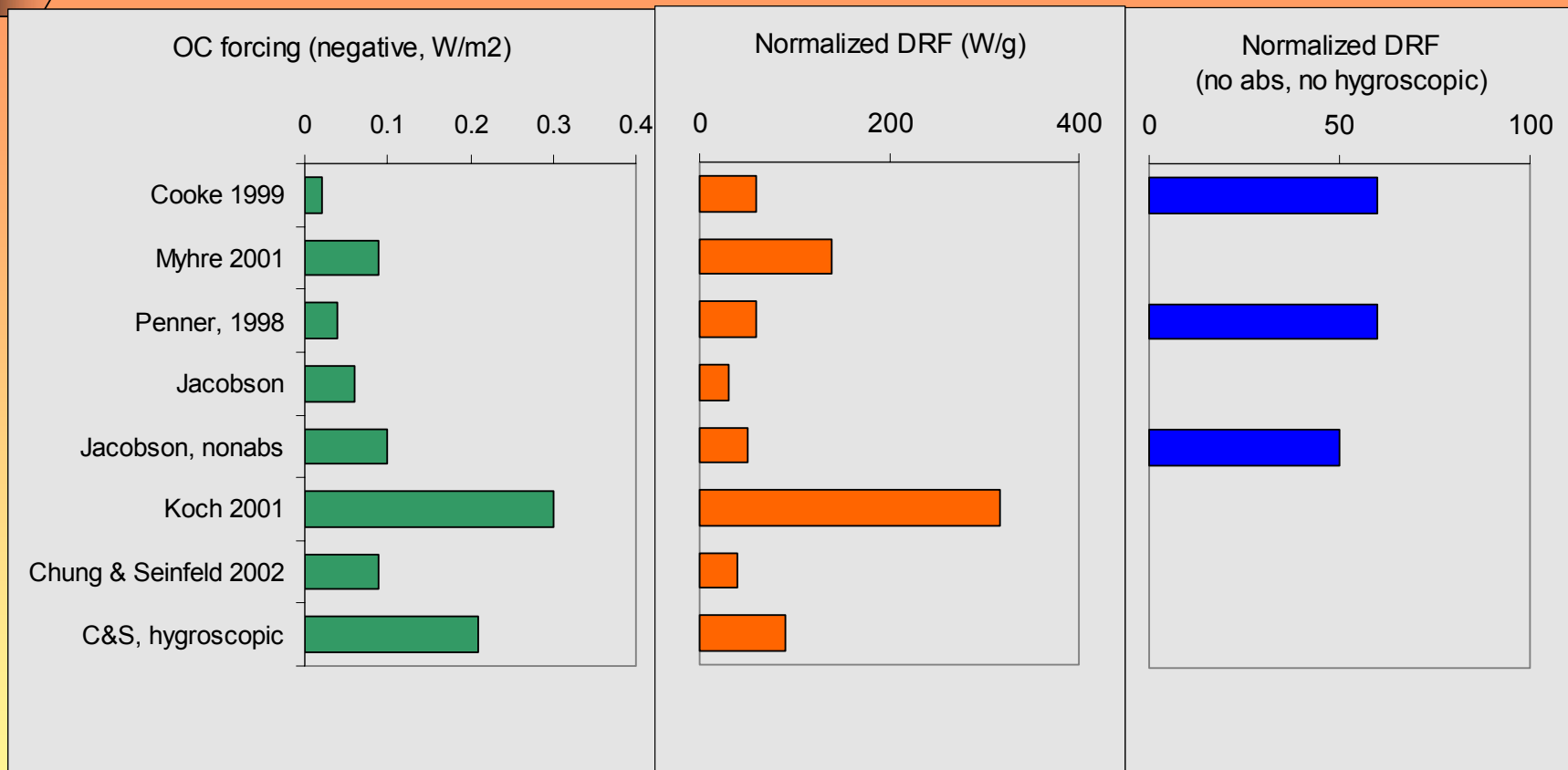
# Variation in model results

Modeled integrated forcing by BC during its lifetime:  
860 MJ/gram emitted (350-2000)

Sources of squared uncertainty



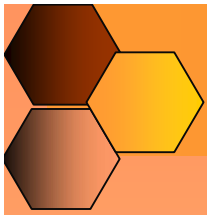
# Model comparisons: organic carbon



coef. var: 83% (unfair)

accounting for emission  
& lifetime differences  
coef. var: 96%

accounting for some  
property differences  
coef. var: 10%



# Indirect forcing: some questions

- ✦ Which aerosols dominate number concentration in critical regions?
  - Primary? (BC, dust, some organic)
  - Precursors of nucleation?
- ✦ Which aerosols/precursors affect cloud droplet number and size?
  - Solubility, or other better metric?



# How defined classes of carbon affect forcing estimates

## *Uncertainties remain in:*

- ✦ Emission estimates  
(what's the conserved quantity?)
- ✦ Model corroboration  
(what's the lifetime?)
- ✦ Species representation  
(what are the properties?)