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Single-Particle Laser-Induced Fluorescence Spectra of Atmospheric Aerosol: Effects of Heating Prior to Measurement

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TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Single-Particle Measurements of Laser-Induced-Fluorescence (LIF) of Background Atmospheric Aerosols

Primary Applications:

-- Rapid, reagentless, detectors for harmful aerosols such as allergens, biowarfare agents, combustion particles (do not identify, but could indicate when to turn on identifiers)

-- Spectra may be useful in designing LIDAR systems.

Particles of interest must be detected against a complex background.

"Signatures" may not be well defined, so differences from background may be useful.

LIF may be useful for studying atmospheric chemistry.

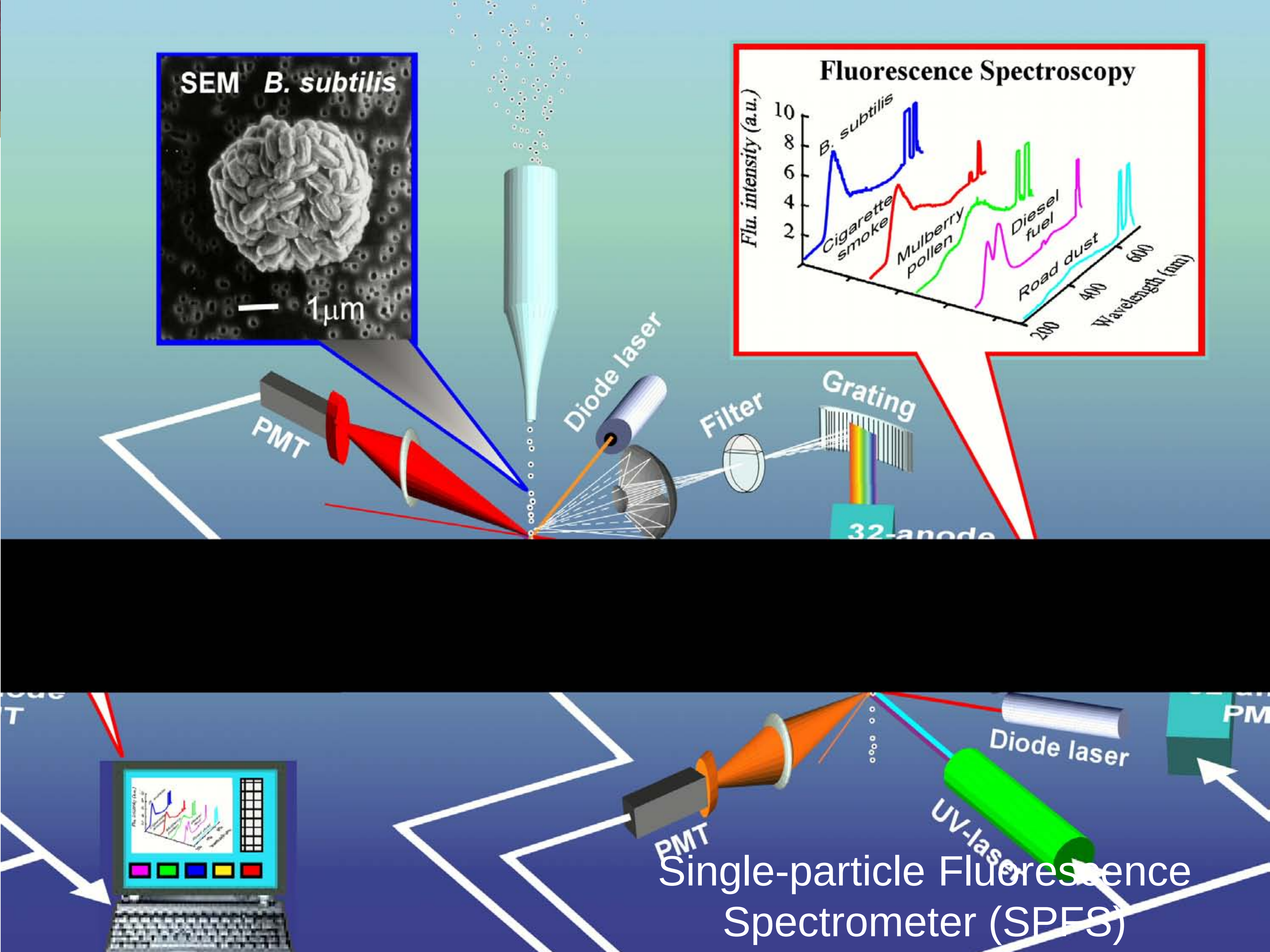
Overview

1) Measurements of UV-LIF spectra of individual atmospheric aerosols at different locations. Classification of LIF spectra using an unstructured cluster analysis.

2) What types of fluorescent molecules or materials occur in atmospheric aerosol?

3) What materials in the atmosphere have spectra similar to the cluster spectra measured?

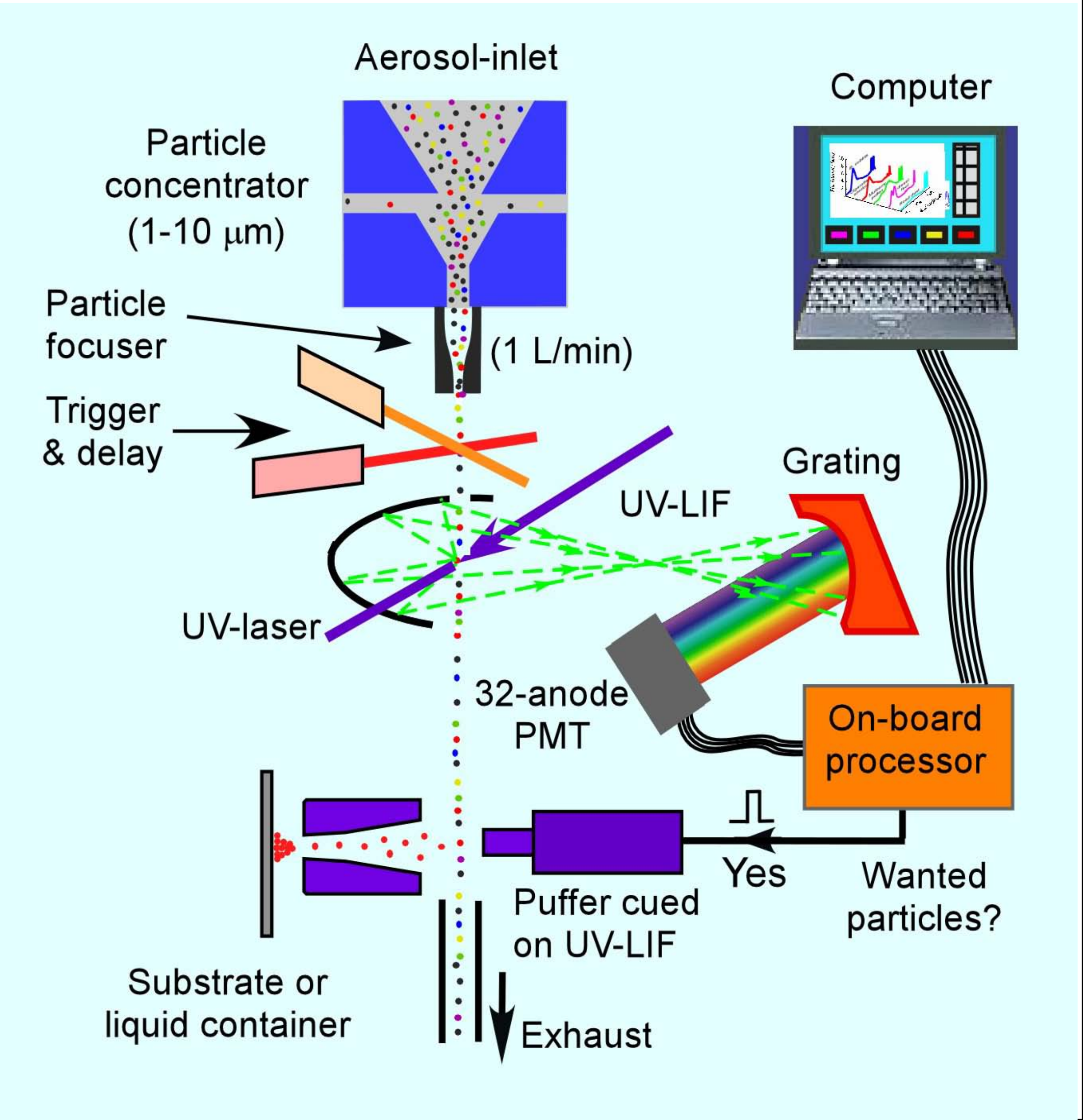
4) Measurement of particle counts in different LIF clusters when particles were heated briefly before being sampled.



Single-particle Fluorescence Spectrometer (SPFS)

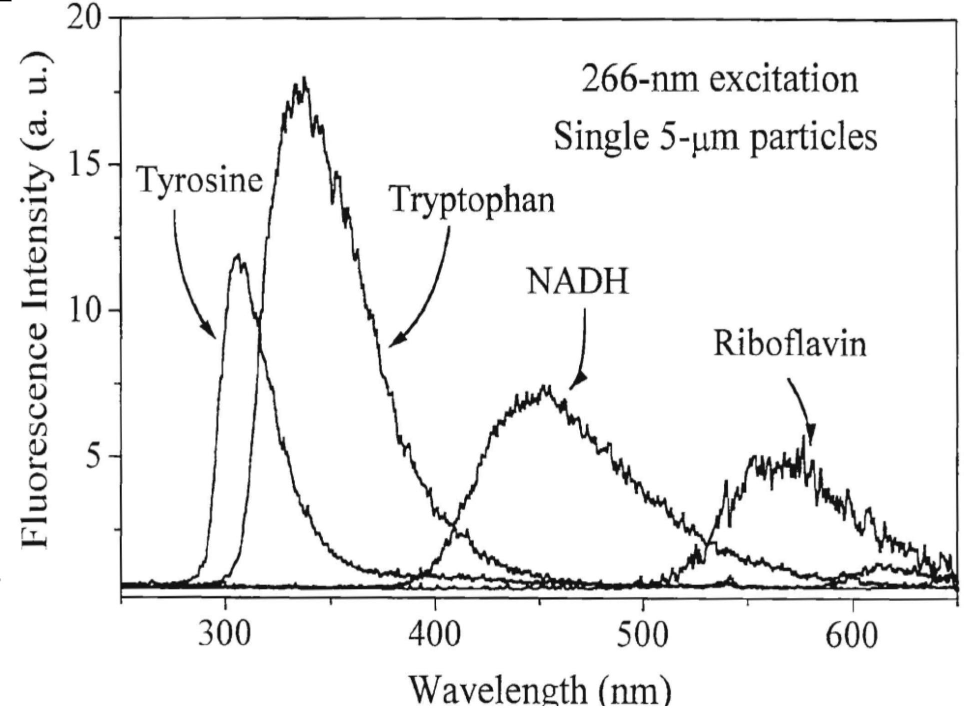
With LIF-Cued Aerodynamic Particle Sorter (Puffer)

Can collect particles with selected LIF spectra for further analysis.

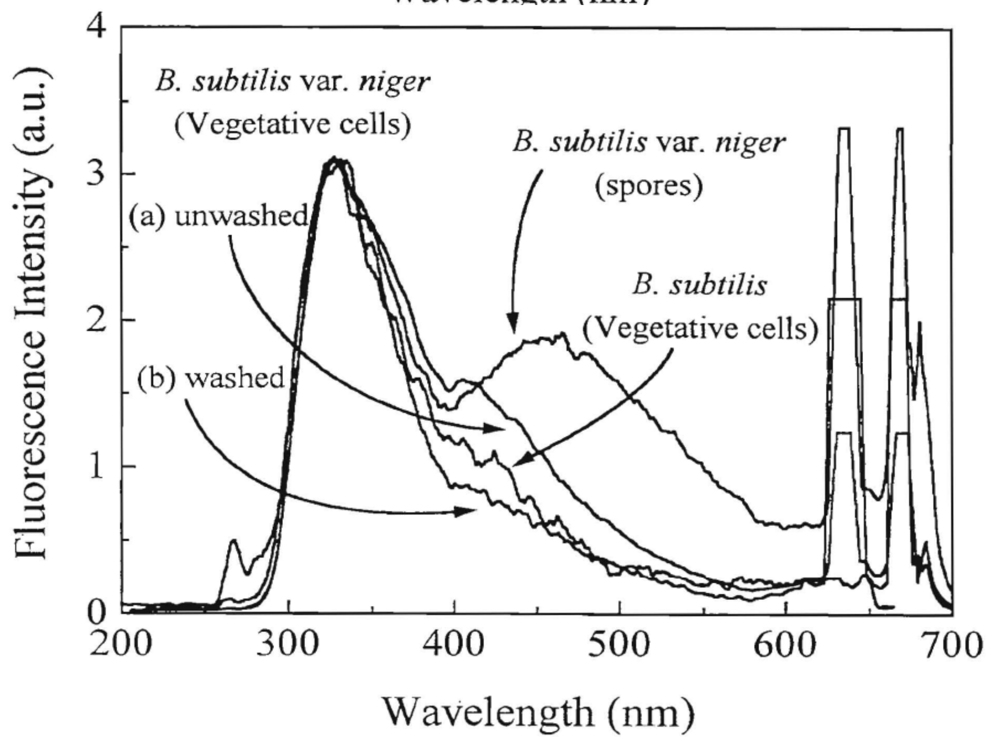


Motivation to measure LIF:
-tryptophan is 1-5% dry weight in bacteria, etc.
-fluorescent quantum efficiency 16%

Fluorescent molecules found in all biological cells

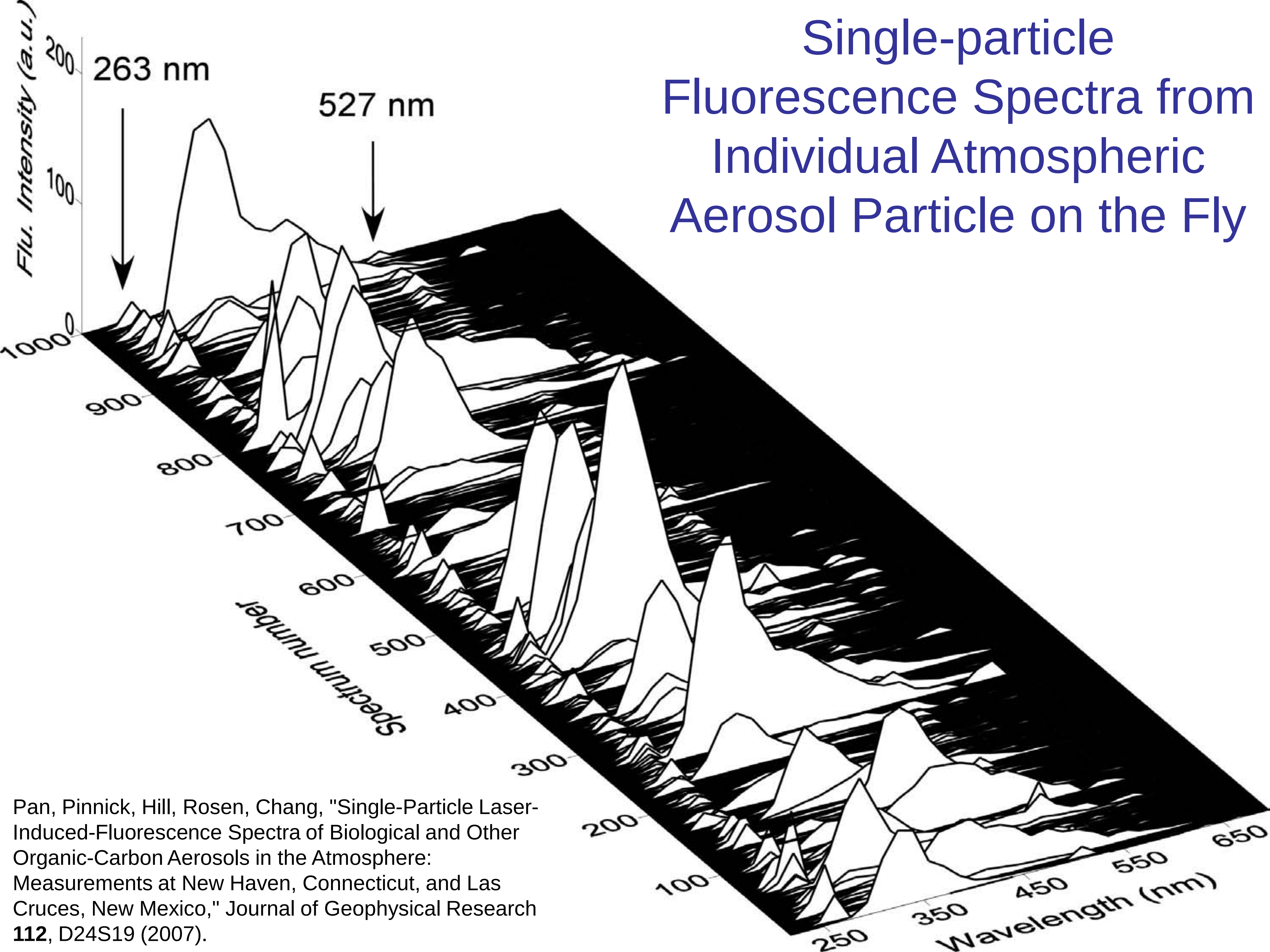


Fluorescence of bacteria depend on the growth media and how well this was removed.



From Hill et al., Field Analytical Chemistry and Technology, 3, 221-239 (1999).

Single-particle Fluorescence Spectra from Individual Atmospheric Aerosol Particle on the Fly



Pan, Pinnick, Hill, Rosen, Chang, "Single-Particle Laser-Induced-Fluorescence Spectra of Biological and Other Organic-Carbon Aerosols in the Atmosphere: Measurements at New Haven, Connecticut, and Las Cruces, New Mexico," Journal of Geophysical Research **112**, D24S19 (2007).

Heirarchical Cluster Analysis of Fluorescence Spectra

1. Fluorescence spectra are corrected for spectral efficiency at different wavelength of detector, grating, and filter.

2. Each spectrum is treated as a n-dimensional vector

$$\mathbf{u} = V\mathbf{v},$$

where $\mathbf{v}$ is normalized ($\mathbf{v} \cdot \mathbf{v}=1$), and

V is the amplitude $V = (\Sigma u_j u_j)^{1/2}$.

3. Unstructured heirarchical cluster analysis:

Combine closest spectra, i.e., those with largest $\mathbf{v}_i \cdot \mathbf{v}_j$

Calculate new average spectrum for this cluster

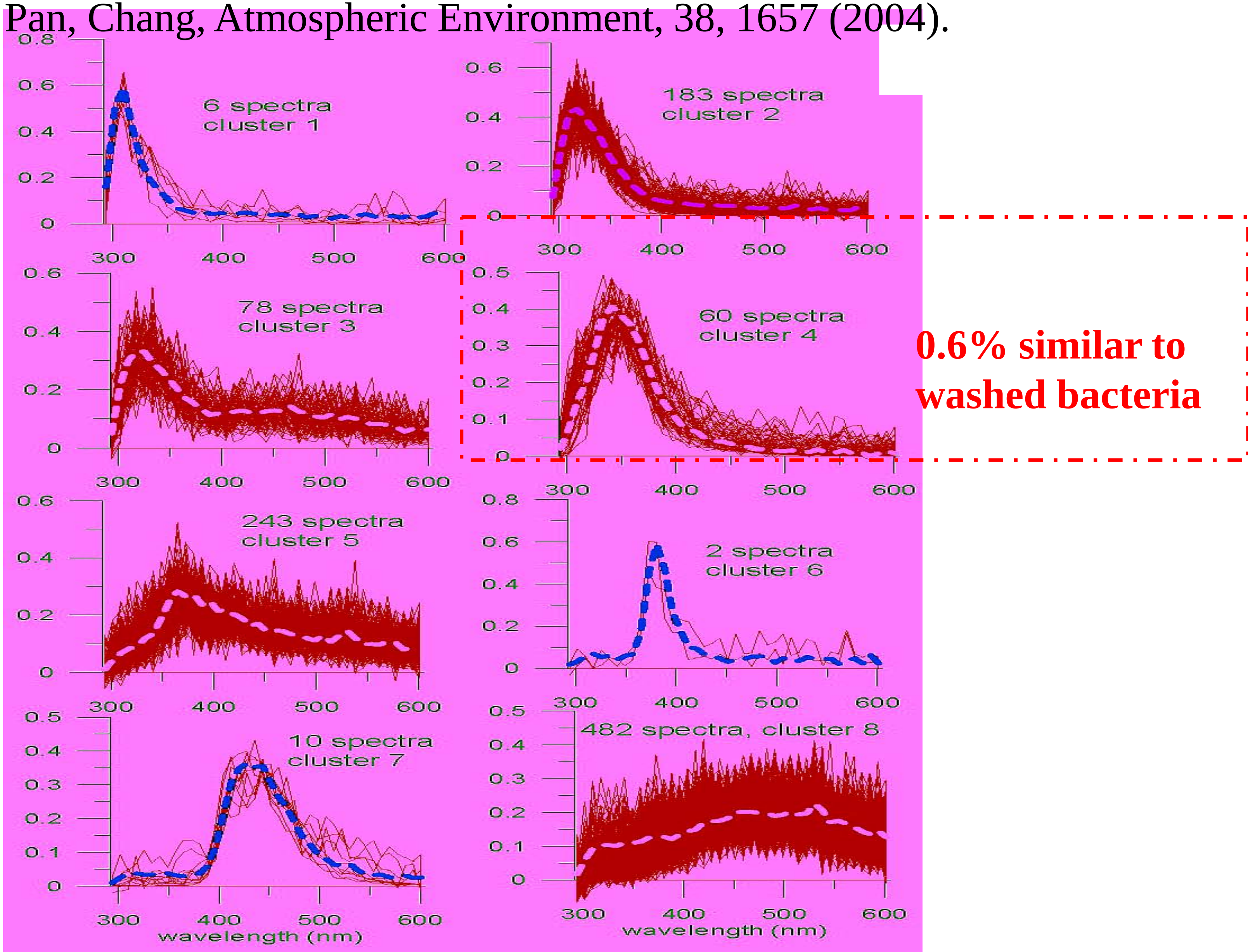
Repeat. Continue to combine spectra until all have

$\mathbf{v}_i \cdot \mathbf{v}_j < 0.9$.

Single ambient particle fluorescence spectrum at Adelphi, MD

130,000 particles, ~8.5% fluoresce, over 90% grouped into 8 clusters, ~0.6% have spectra similar to washed bacteria.

Pinnick, Hill, Pan, Chang, Atmospheric Environment, 38, 1657 (2004).



If measure LIF spectra of atmospheric aerosols

in other locations (different climate),

at different times of year,

with a different instrument,

will the clusters found be similar?

If clusters are similar, are percentages in the clusters similar at different locations?

Maryland, Potomac River

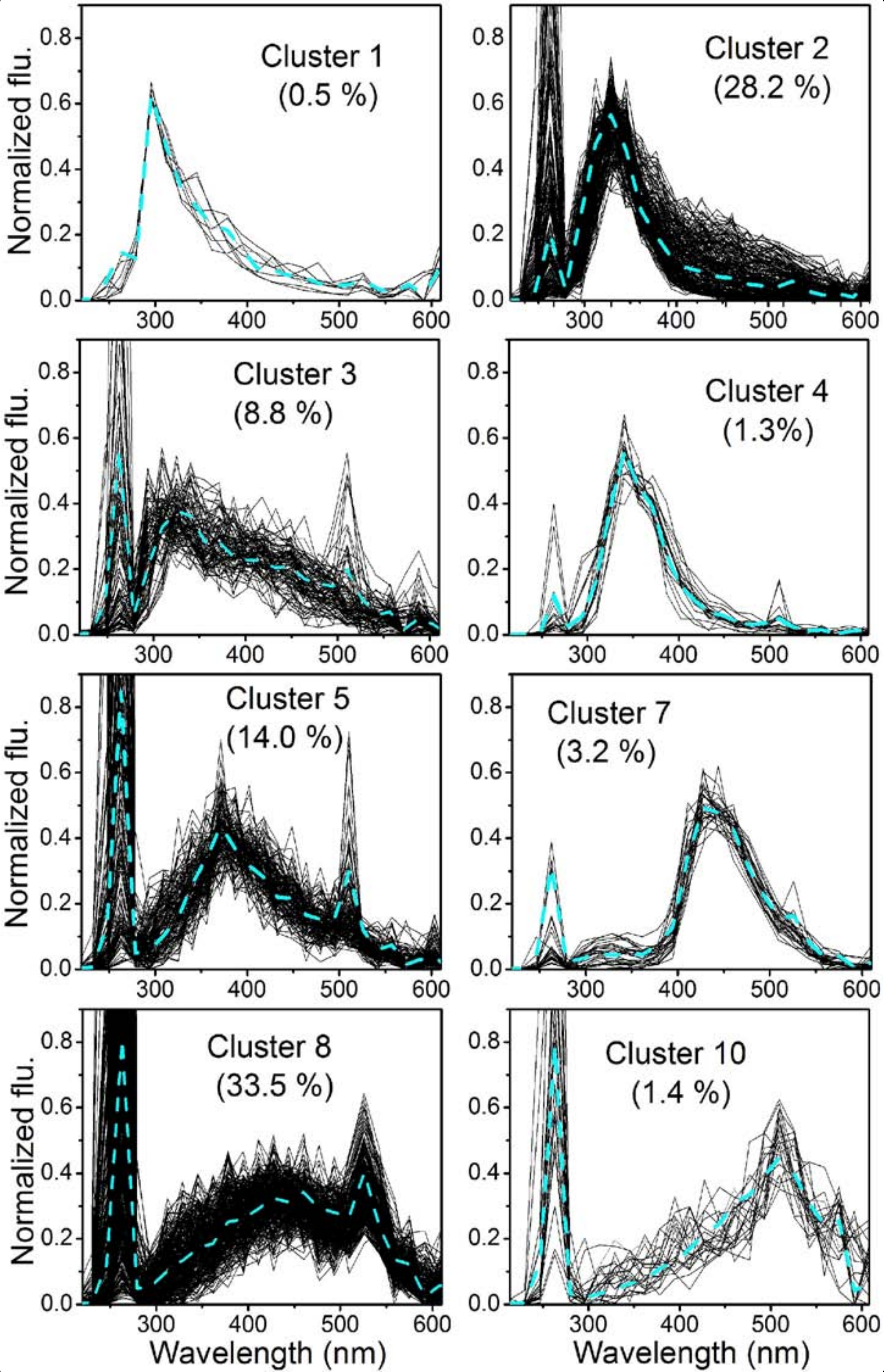
Near our sampling site at Adelphi.

Vegetation has many similarities to that in New Haven, CT.

New Mexico
Near Las Cruces
Chihuahuan Desert

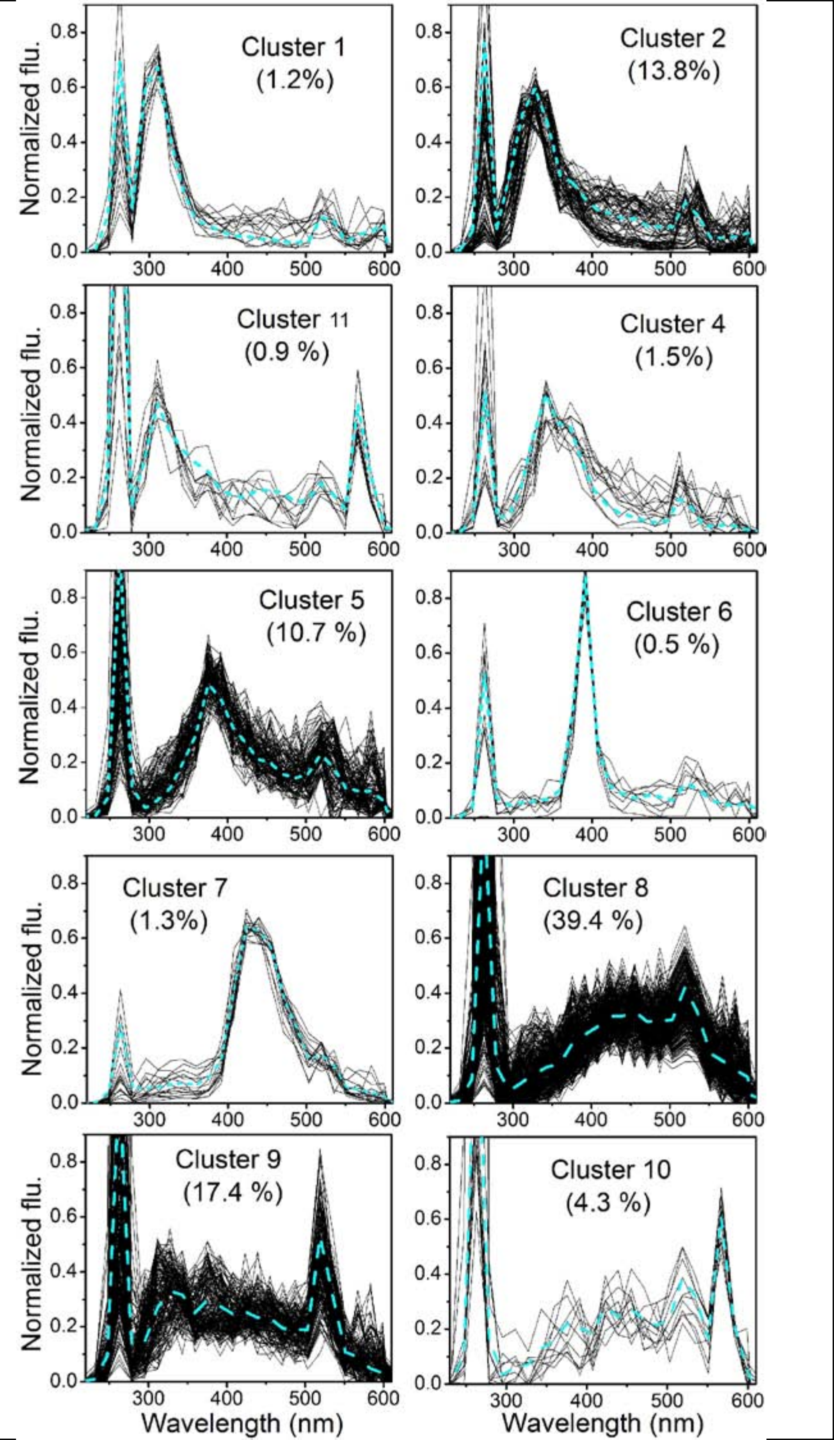
Normalized fluorescence spectra of single atmospheric aerosol particles measured at
New Haven, CT

Dotted lines are average spectra for each cluster



Normalized fluorescence spectra of single atmospheric aerosol particles measured at Las Cruces, New Mexico

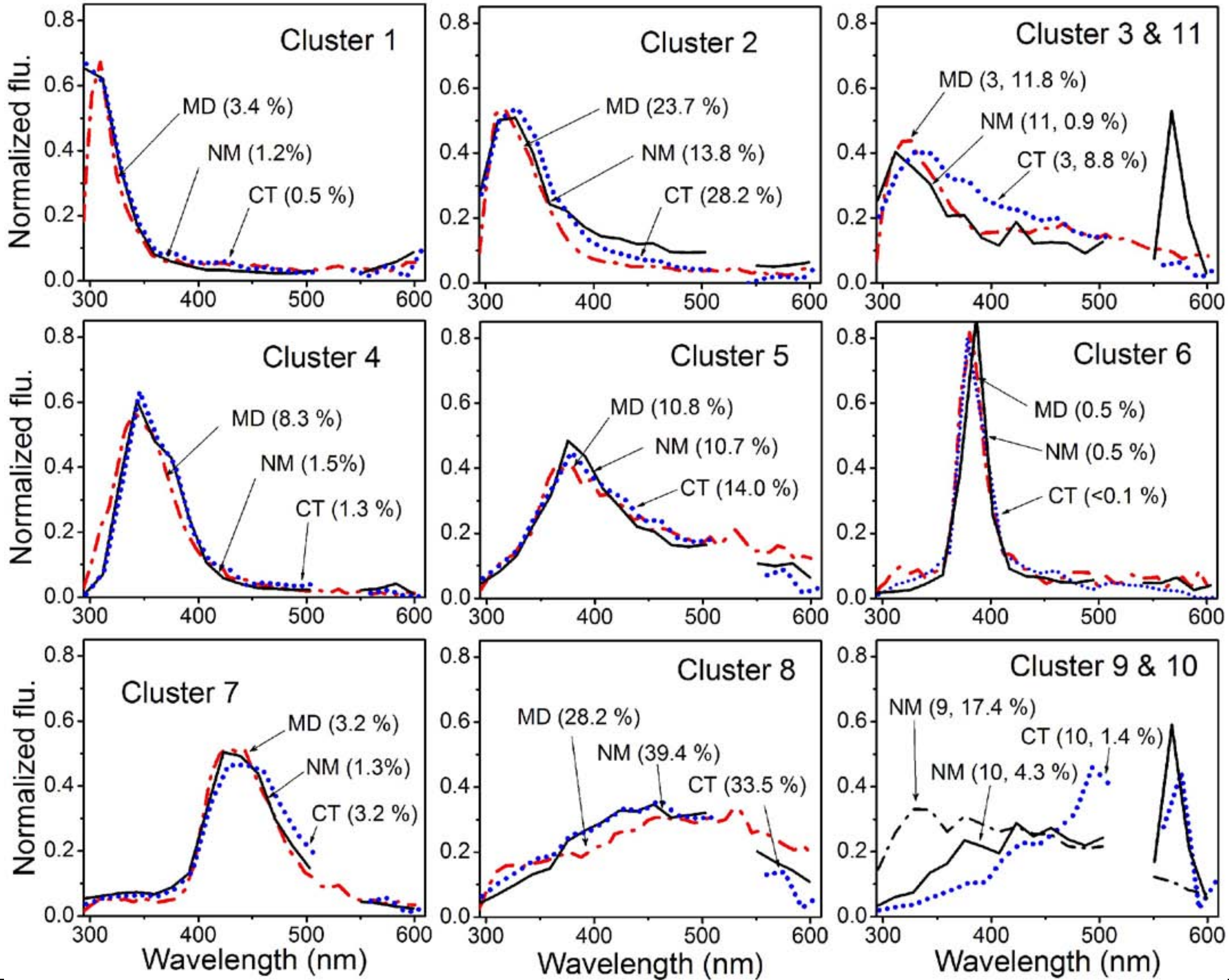
Dotted lines are average spectra for each cluster



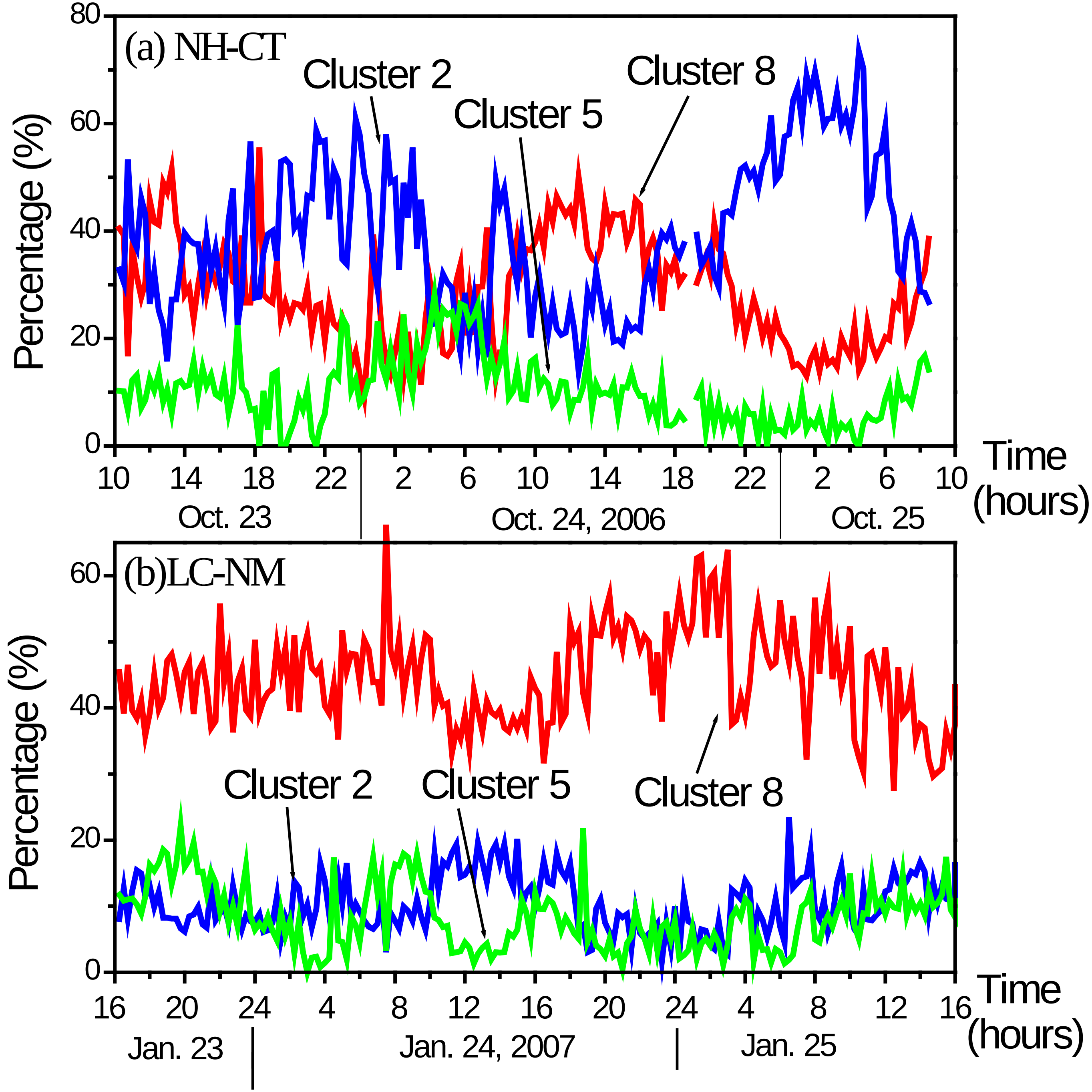
Fluorescence spectra templates derived from hierarchical cluster analyses run independently at each location.

Similar clusters appear at Adelphi, MD, New Haven, Las Cruces, NM

Most highly populated clusters are cluster 8, 2, and 5.



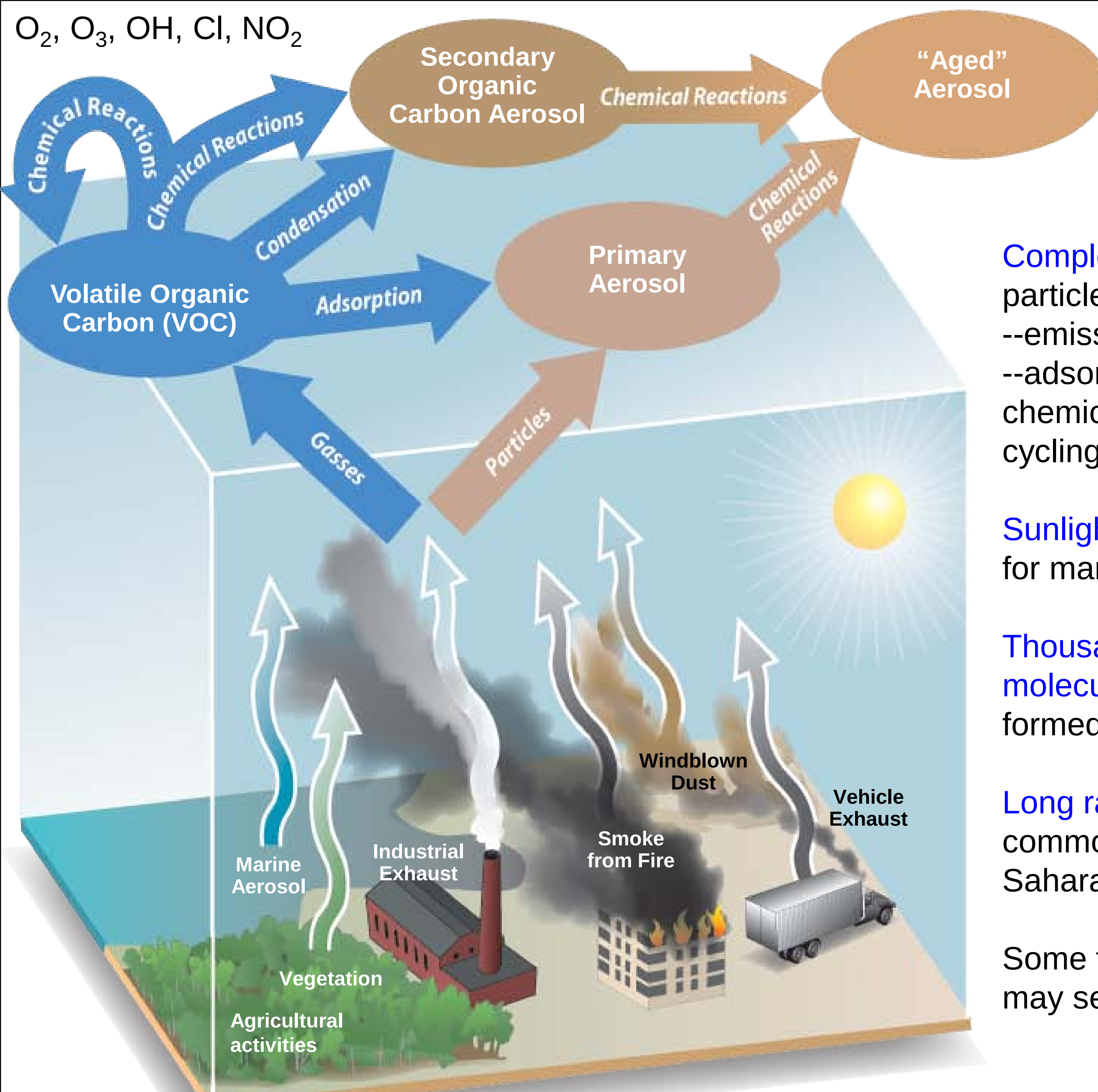
Pan, et al., J. Geophys. Res., 112, D24S19, 28 Dec., 2007.



(a) NH-CT
Cluster 2
Cluster 5
Cluster 8
Percentage (%)
0
20
40
60
80
10
14
18
22
2
6
10
14
18
22
2
6
10
Time (hours)
Oct. 23
Oct. 24, 2006
Oct. 25
(b)LC-NM
Cluster 2
Cluster 5
Cluster 8
Percentage (%)
0
20
40
60
16
20
24
4
8
12
16
20
24
4
8
12
16
Time (hours)
Jan. 23
Jan. 24, 2007
Jan. 25

What types of fluorescent molecules or materials occur in atmospheric aerosol?

Atmospheric Aerosol is Extremely Complex



Complex mixtures can occur in particles because of
--emission of complex particles
--adsorption, agglomeration, chemical reactions, and cycling through clouds.

Sunlight provides the energy for many chemical reactions.

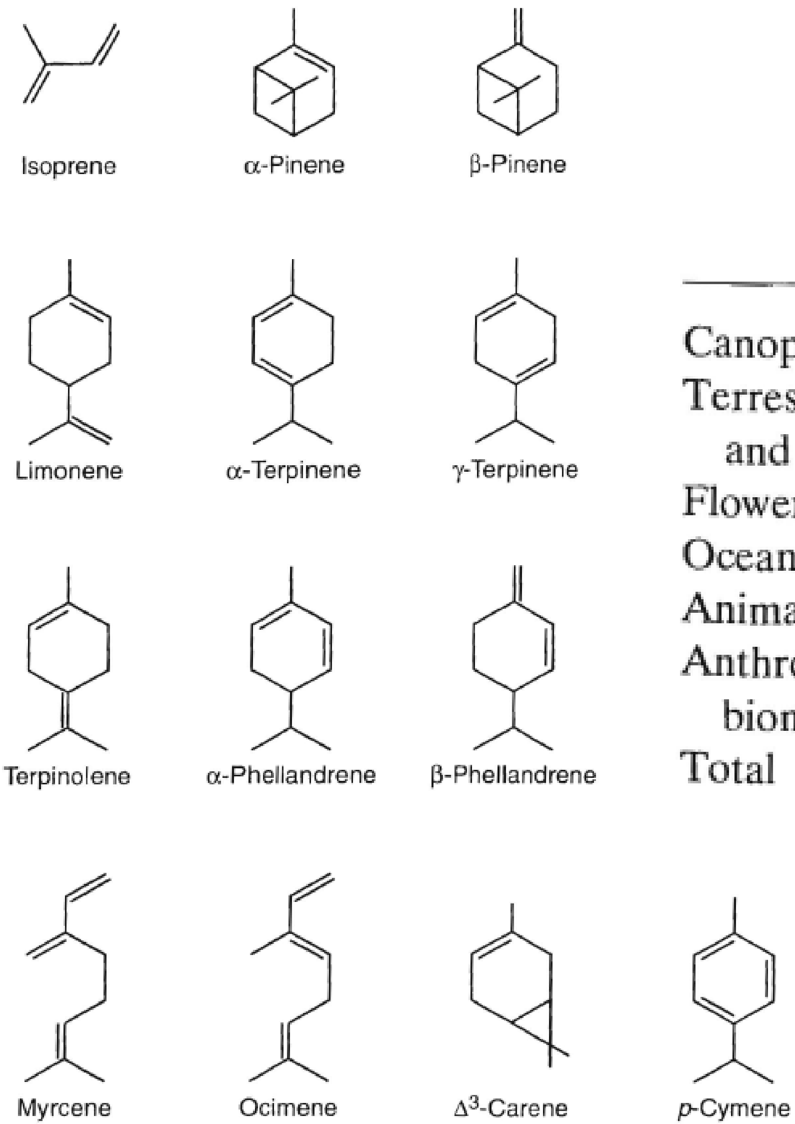
Thousands of fluorescent molecules are emitted and formed in chemical reactions.

Long range transport is common: China → California, Sahara Desert → Carolinas

Some fluorescent compounds may serve as tracers.

Terpenes – emitted from plants, can polymerize to form particles

Example monoterpenes



Estimated Global Annual Biogenic Volatile Organic Carbon (VOC) Emissions (Tg yr^{-1})

Source	Isoprene	Monoterpenes	Other VOCs[b]
Canopy foliage	460	115	500
Terrestrial ground cover and soils	40	13	50
Flowers	0	2	2
Ocean and freshwater	1	<0.001	10
Animals, humans, and insects	0.003	<0.001	0.003
Anthropogenic (including biomass burning)	0.01	1	93
Total	~500	~130	~650

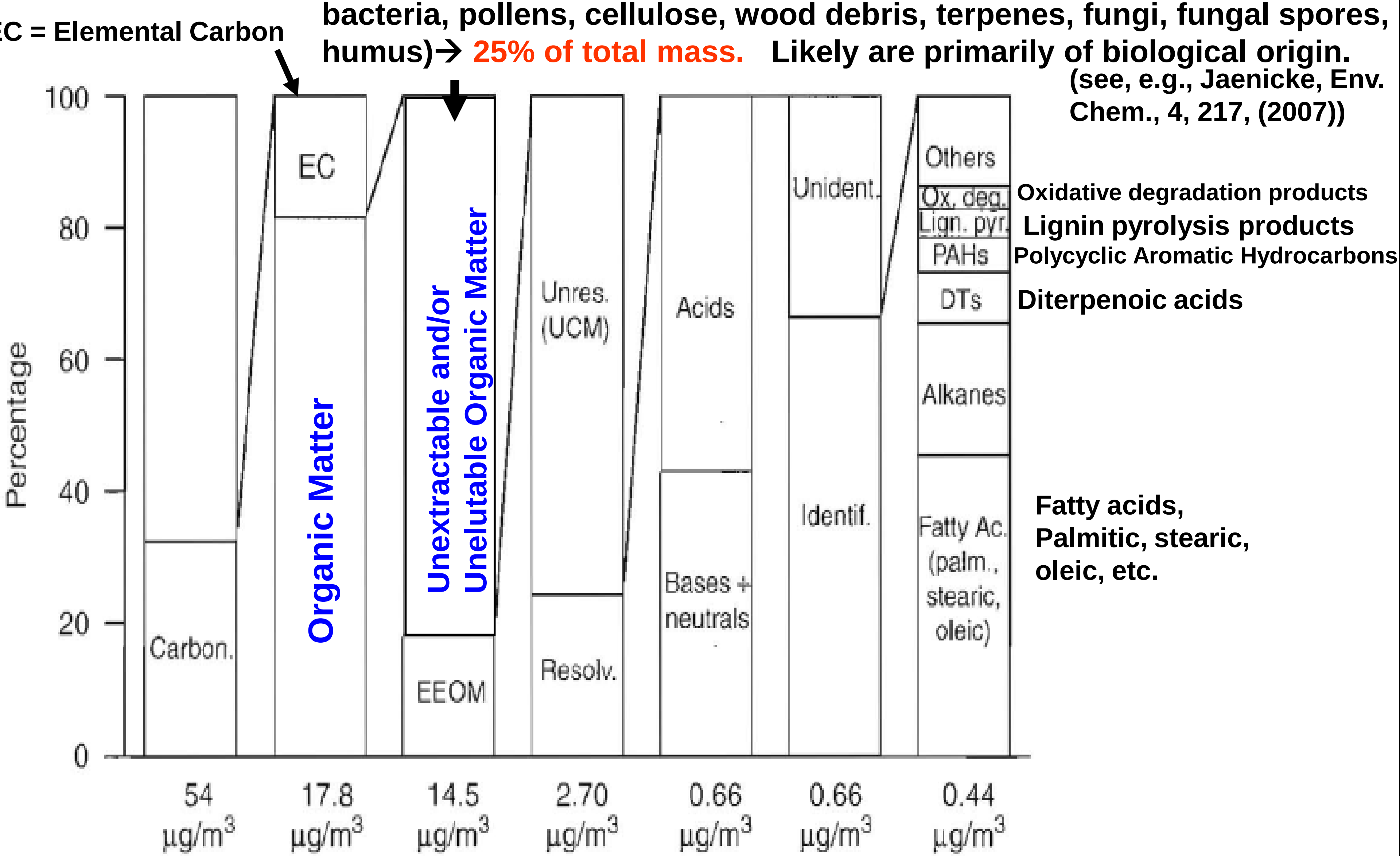
Other VOCs include all volatile organic compounds other than methane, isoprene, and monoterpenes

From Finlayson-Pitts and Pitts, *Chemistry of Upper and Lower Atmosphere*, (Academic, 2000), p. 226-227, who used data from Guenther and others..

Most of these would not fluoresce with 266-nm excitation. Cymene should fluoresce similarly to benzene or styrene.

Unextractable and/or Unelutable Organic Matter (leaf debris, spores, bacteria, pollens, cellulose, wood debris, terpenes, fungi, fungal spores, humus)→ 25% of total mass. Likely are primarily of biological origin.

(see, e.g., Jaenicke, Env. Chem., 4, 217, (2007))



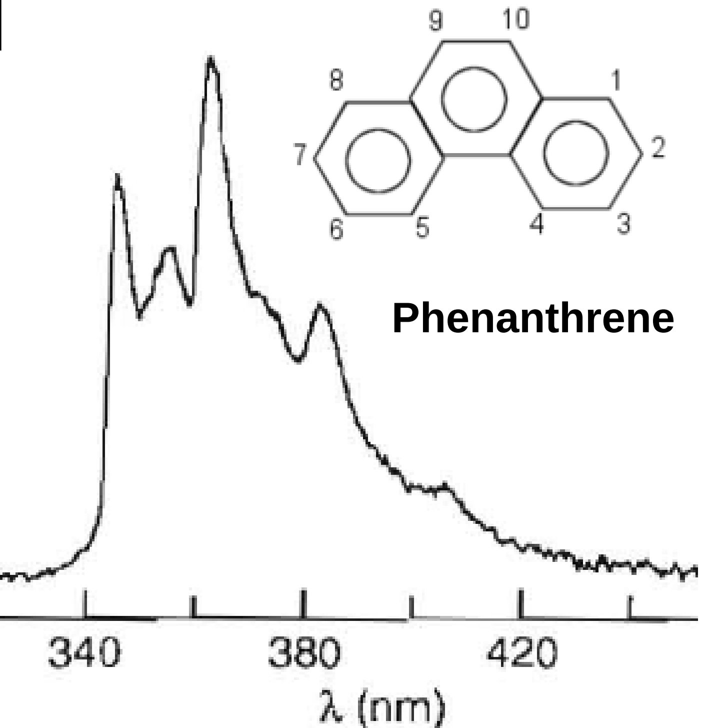
ubatova, et al., (2002), "Organic compounds in urban aerosols from Gent, Belgium: haracterization, sources, and seasonal differences," J. Geophys. Res. Atmos., 107, D21,8343.

Fluorescent Molecules in the Atmosphere

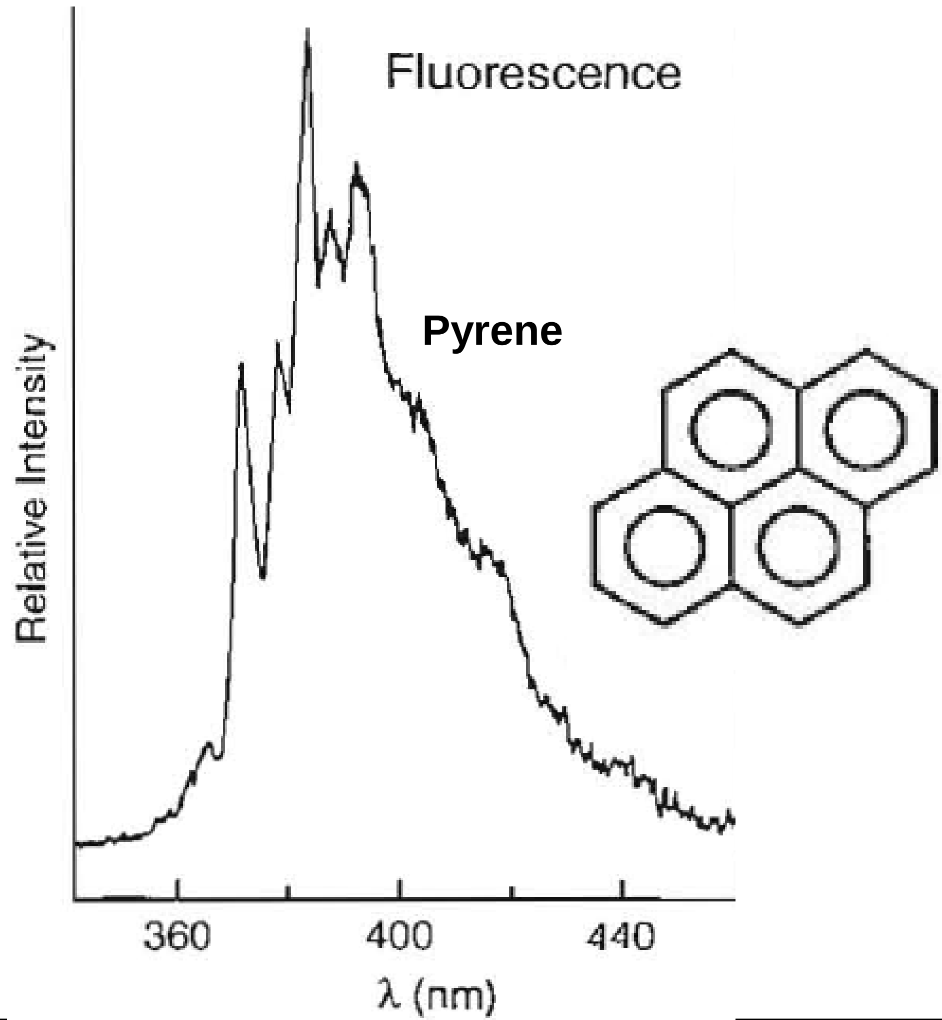
Aromatic (with some exceptions, e.g., chlorophylls)

Polycyclic Aromatic Hydrocarbons (PAH)

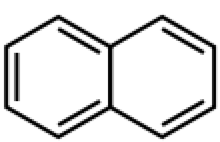
Spectra of PAH shown here from:
Karcher et al., 1985, as shown in Finlayson-Pitts and Pitts, *Chemistry of Upper and Lower Atmosphere*, (Academic, 2000).
Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules (Academic, 1971).



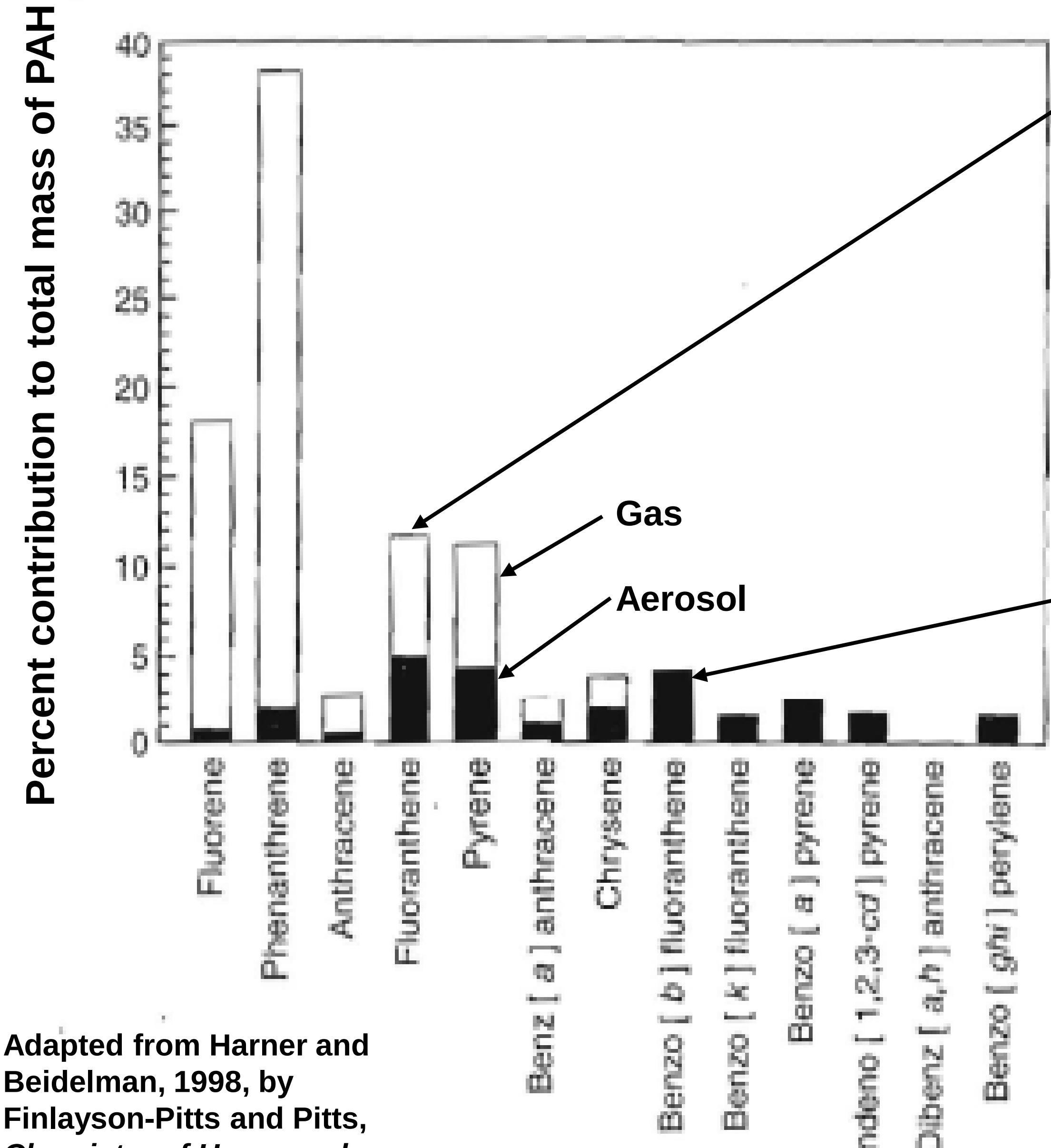
Phenanthrene

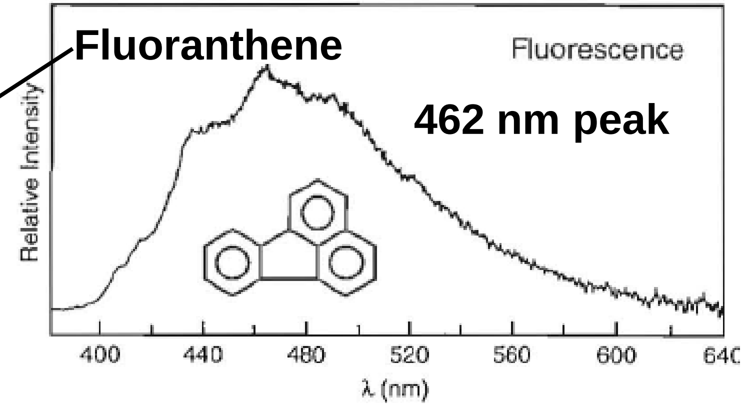


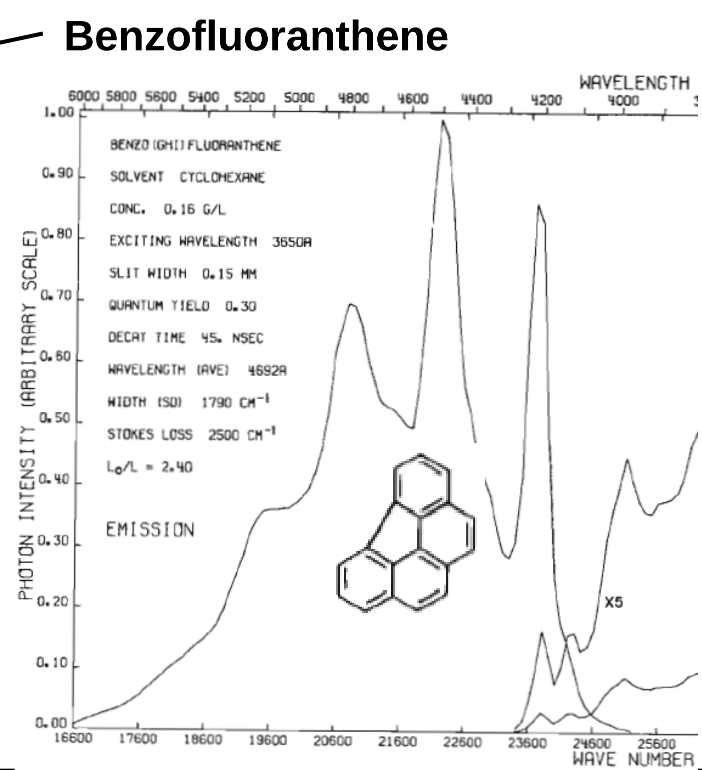
Pyrene



Napthalene fluorescence can be similar to tryptophan.
Too volatile to stay in particles



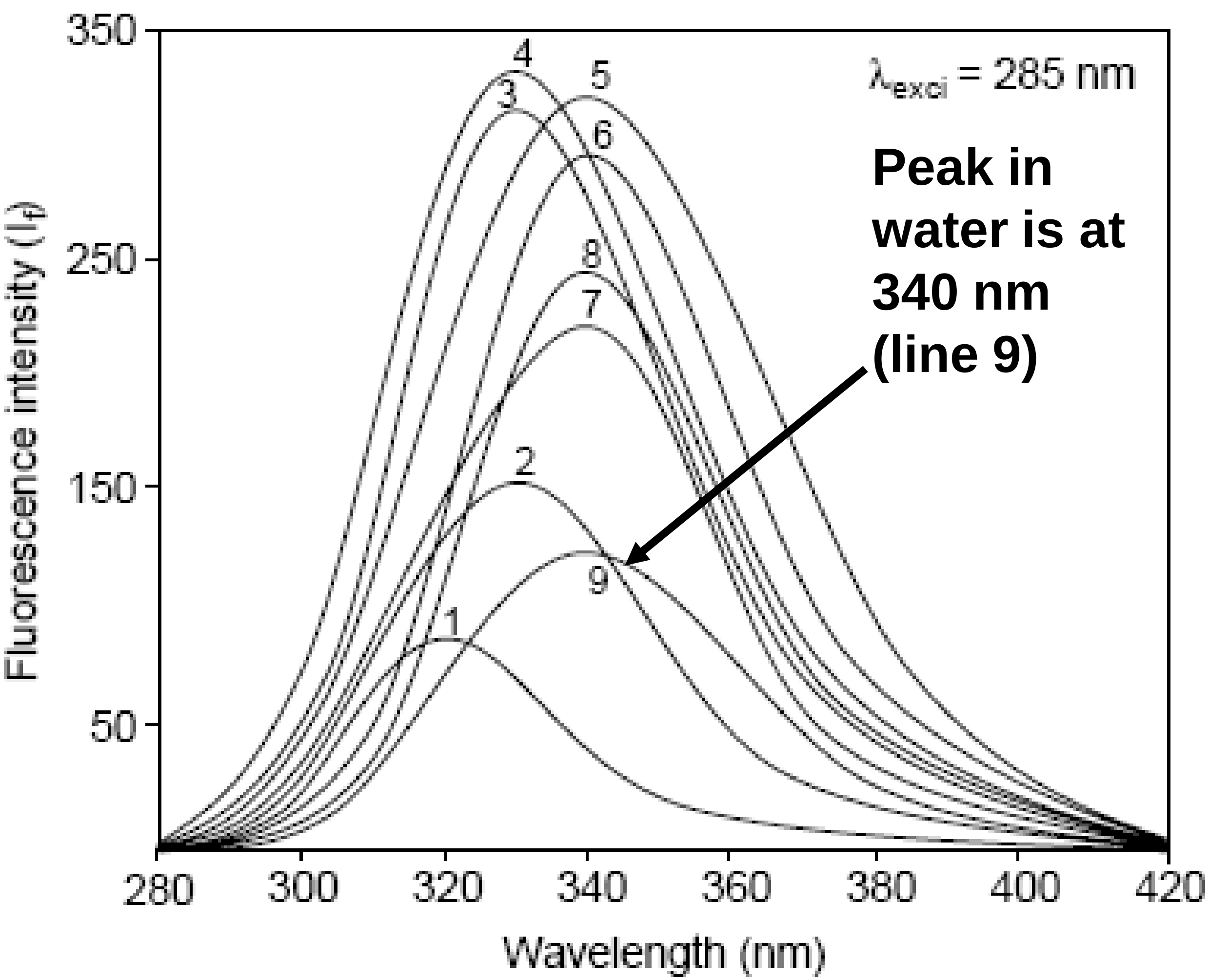


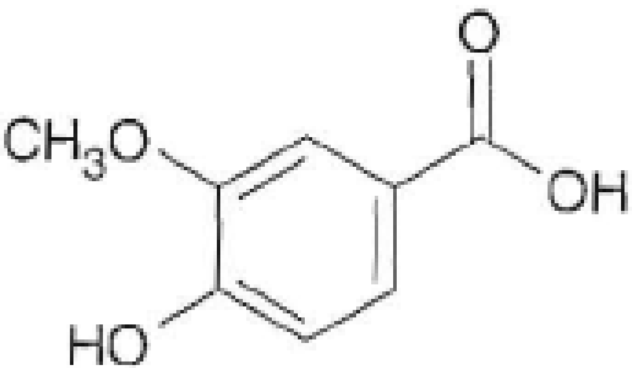


Adapted from Harner and Beidelman, 1998, by Finlayson-Pitts and Pitts, *Chemistry of Upper and Lower Atmosphere*, (Academic, 2000), p. 456.

Vanillic acid – tracer for biomass burning

Fluorescence spectrum very similar to tryptophan

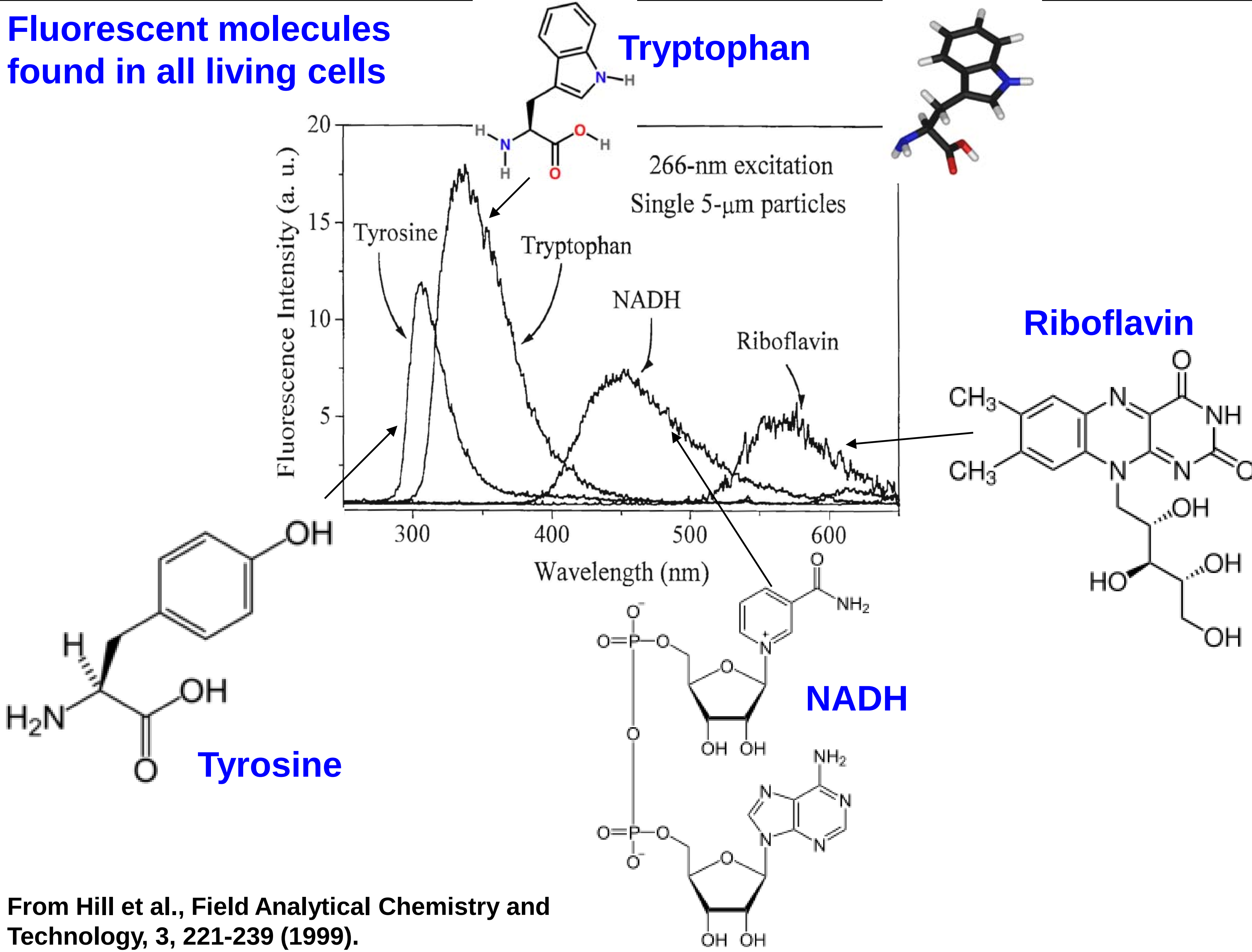




Vanillic acid

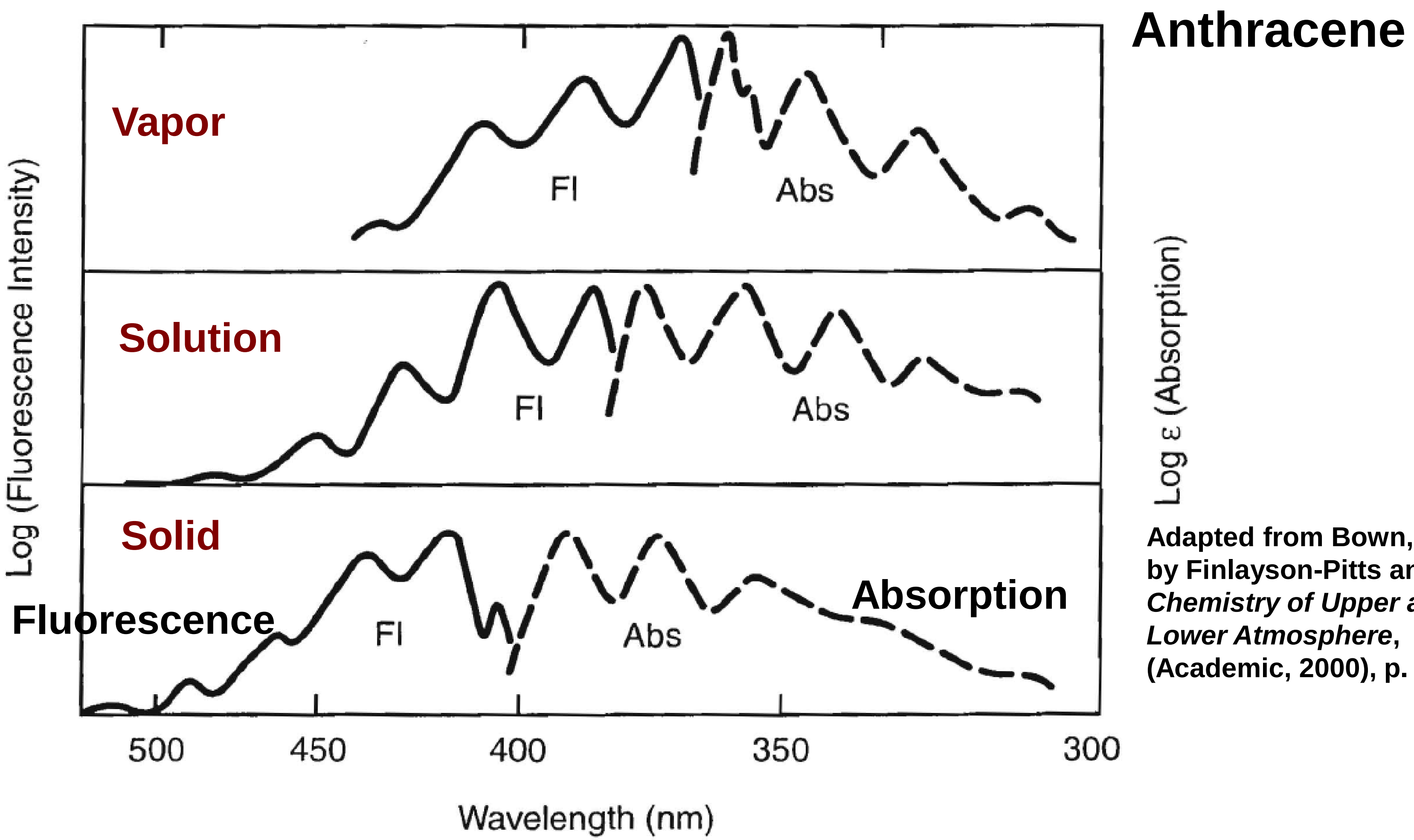
Peak emission depends on the local environment (solvent here).

Fluorescent molecules found in all living cells



From Hill et al., Field Analytical Chemistry and Technology, 3, 221-239 (1999).

Peak Fluorescence Emission Shifts to Longer Wavelengths in Going from Vapor to Solution to Solid

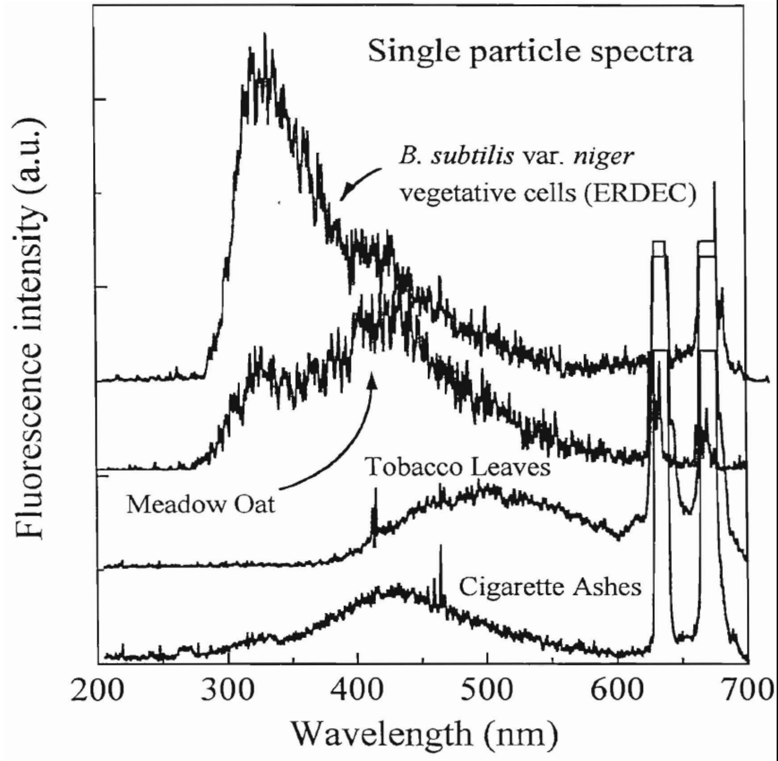


Adapted from Bown, 1946, by Finlayson-Pitts and Pitts, *Chemistry of Upper and Lower Atmosphere*, (Academic, 2000), p. 465.

Also, riboflavin's peak fluorescence shifts from 515 nm in a droplet to 560 nm in a solid particle.

Fluorescent Materials of Biological Origin (beyond tryptophan, NADH, flavins)
- where it may not be clear what the fluorescent molecules are.

Cellulose (ferulic acid is likely)
Pollen (meadow oat)
Fungal spores
Wood (lignins, lignans, sinapyl alcohol, coniferyl alcohol)
Fungi breaking down wood (hyphae)
Dissolved organic matter (decomposing leaves in water, phenols, polyphenols, coumarins)
Humic substances, humic acids
Fulvic acids

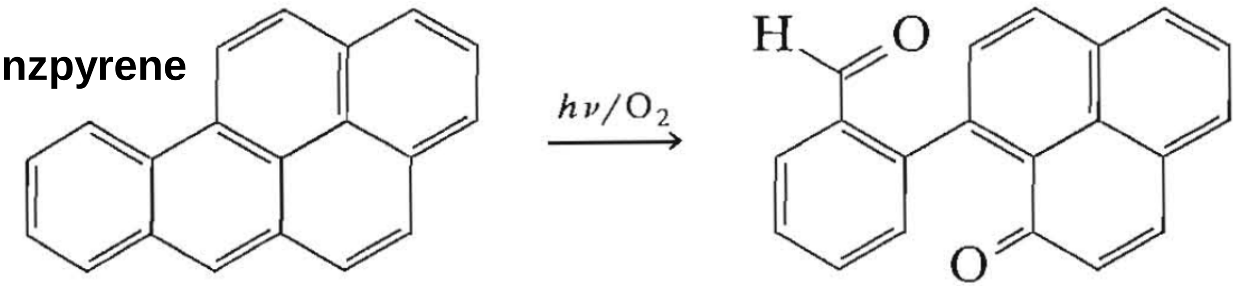


From Hill et al., Field Analytical Chemistry and Technology, 3, 221-239 (1999).

Example Chemical Reactions of Molecules in the Atmosphere that Generate Additional Fluorescent Molecules

Oxidation

Benzpyrene

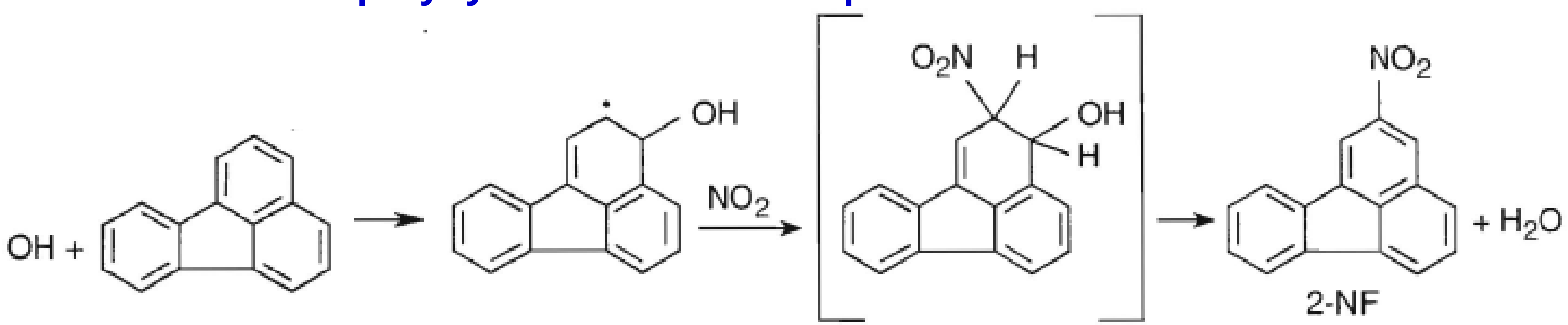


Oxidation can decrease the conjugation and shift spectra to shorter wavelengths

Napthalene
too volatile to be primarily in particles.

Phthalic acid
Its salts are not volatile.
Slightly soluble in water.

Oxidation by nitrogen dioxide, initiated by OH.
Nitro-substituted polycyclic aromatic compounds tend to fluoresce less or not at all.



Fluorescent Molecules in the Atmosphere

1. Have conjugated double bonds, mostly Aromatic.

2. Fluorescence shifts to longer wavelengths as length/area of conjugated bonds increases (Schrodinger box).

3. Local environments affect fluorescence: emissions tend to longer wavelengths as move from solution → solid.

4. Can be formed via chemical reactions in the atmosphere mostly from other fluorescent molecules. Large PAH may be oxidized (oxygen, ozone) to smaller, more-soluble-in-water aromatics that can fluoresce at shorter wavelengths.

5. Materials of biological origin account for a large fraction (20%?) of the mass of atmospheric aerosol. There are many non-tryptophan fluorophores in: leaf debris, spores, bacteria, pollens, cellulose, wood debris, fungi, fungal spores, humus.

What types of fluorescent molecules or materials:

a) occur in atmospheric aerosol, and,

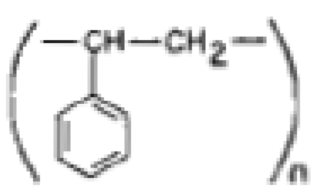
b) have spectra similar to the clusters we measured?

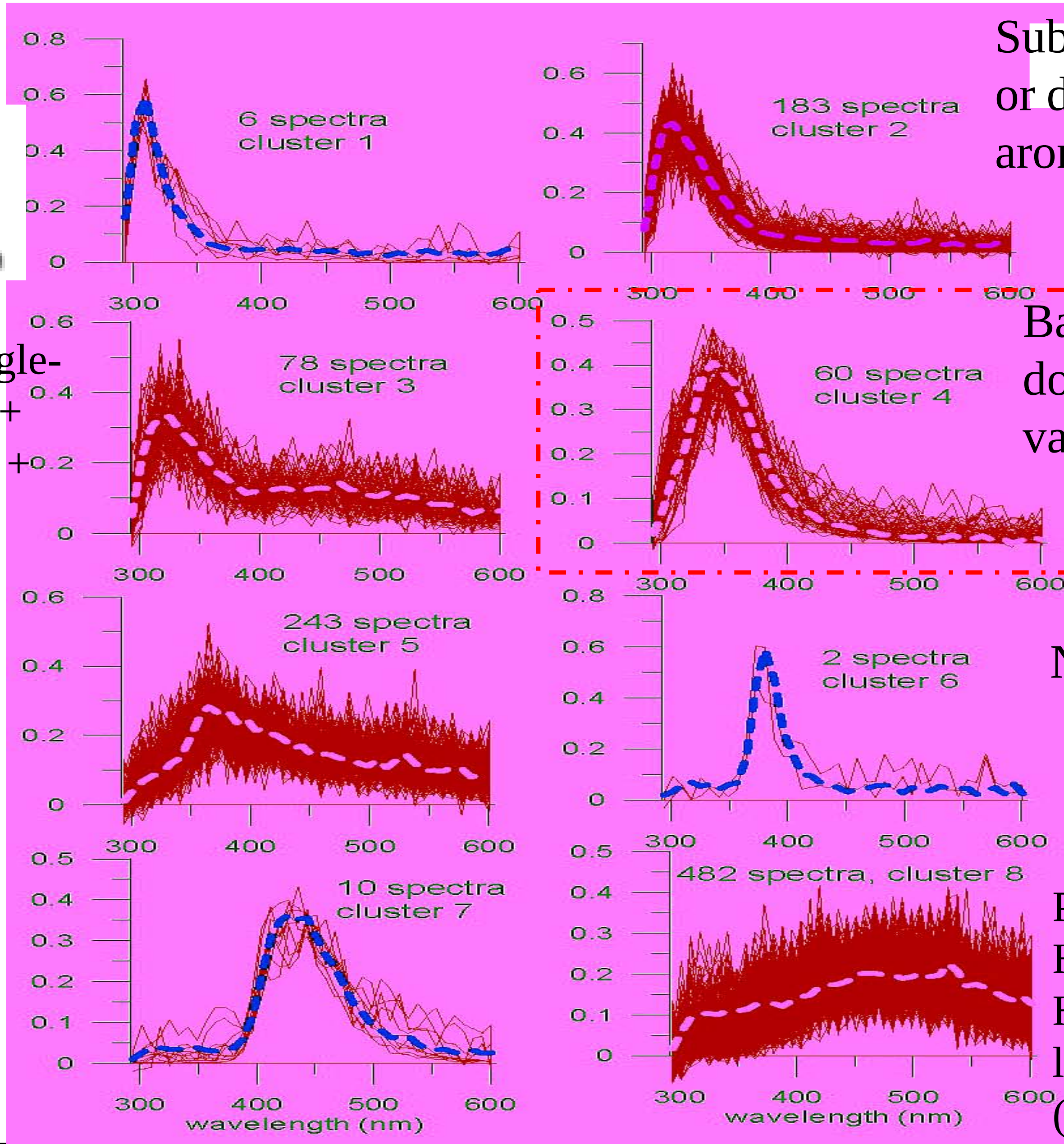
More measurements of fluorescence spectra of known materials could be useful (excitation/emission).

Ambient particle fluorescence spectra at Adelphi, MD. Dotted lines are averages.

Some materials in atmospheric aerosol that have similar spectra are listed.

Single-ring aromatics -





Substituted single-ring or double-ring aromatics

Substituted single-ring aromatics + Humic/HULIS + protein?

Bacteria, proteins, double-ring aromatics, vanillic acid

0.6% similar to washed bacteria

Marine aerosol, bacteria

No examples we kno

Cellulose, ferulic acid

Polycyclic Aromatic Hydrocarbons (PAH) Humic acids, Humic-like substances (HULIS)

Percentages of different clusters of fluorescence spectra in different locations

Cluster annotations: 2 – Substituted single-ring or double-ring aromatics; 4 – Bacteria, proteins; 5 – Marine aerosol; 7 – Cellulose; 8 – Polycyclic Aromatic Hydrocarbons (PAH) Humic acids, Humic-like substances (HULIS)

Clusters	1	2	3	4	5	6	7	8
MD(%, >3μm)	3.4	23.7	11.8	8.3	10.8	0.5	3.2	28.2
NM(%, >3μm)	1.2	13.8	<0.5	1.5	10.7	0.5	1.3	39.4
NM(%, <3μm)	0.6	8.6	<0.5	2.9	12.6	1.9	0.3	44.5
CT (%, >3μm)	0.5	28.2	8.8	1.3	14.0	0.05	3.2	33.5
CT (%, <3μm)	0.3	37.8	5.0	6.3	11.5	0.01	1.7	25.1

Clusters	9	10	11	not fit	flu (%)	Total
MD(%, >3μm)	<0.5	<0.5	<0.5	10.2	11,050 (8.5%)	130,000
NM(%, >3μm)	17.4	4.3	0.9	9.0	10,157 (17.4%)	58,260
NM(%, <3μm)	11.2	5.6	0.9	10.9	13,703 (4.5%)	305,586
CT (%, >3μm)	<0.5	1.4	<0.5	9.1	10,367 (49.3%)	21,007
CT (%, <3μm)	<0.5	2.2	<0.5	10.1	16,892 (16.3%)	103,411

With atmospheric chemistry so complicated, why do most particles go into similar clusters at such diverse locations?

Long range transport?
Similar sources and chemistry?
Similar metabolic degradation pathways?
Thousands of fluors, some dominate?
Ratios of fluors are similar?

Maryland, Potomac River

New Mexico
Chihuahuan Desert

Effects of Heating Prior to Measurement

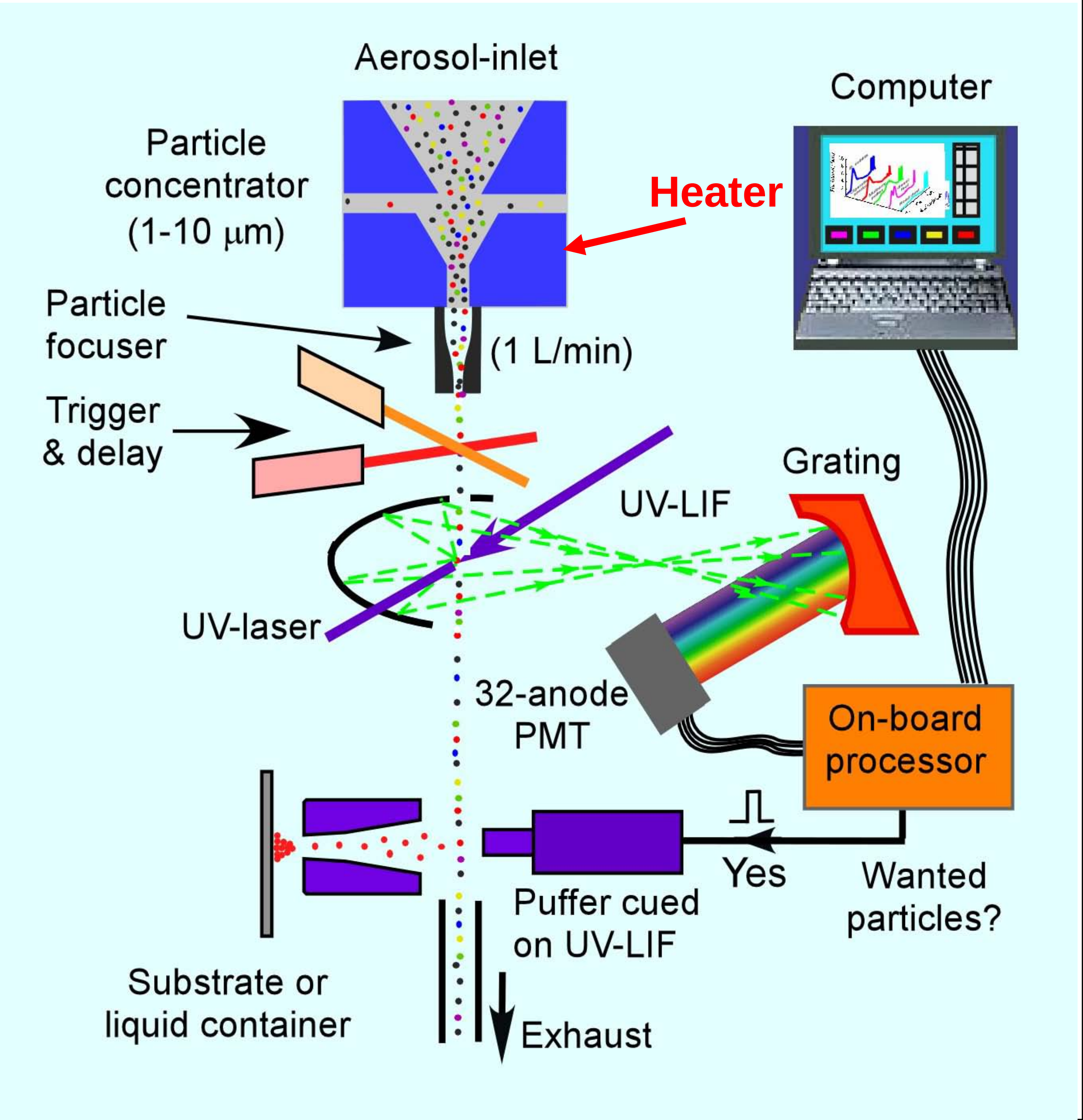
Measurement of particle counts in different LIF clusters when particles are heated briefly before being sampled.

Particle temperature returns to near ambient by the time of measurement

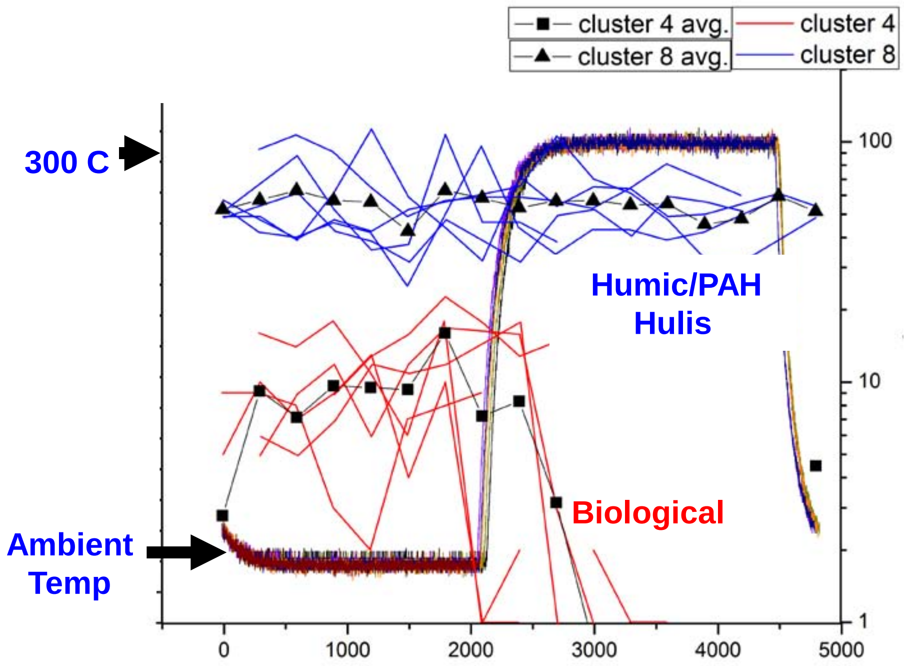
Heat Particles Before LIF Measurement

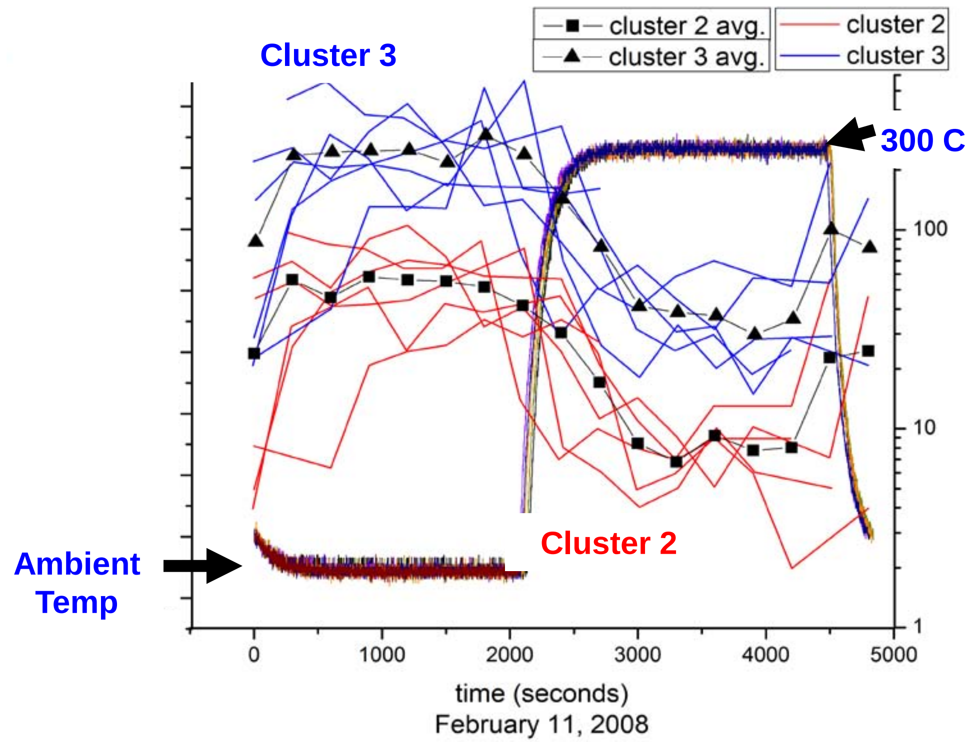
Can heating the particles help determine what materials/fluorophors are in the particles?

Is there a temperature where many interfering particles disappear, but biological aerosols remain? Might heating be used reduce the “uninteresting” particles?



LIF of Heated Particles





Ambient concentrations vary with time, so → repeat the heat cycle 6 times

Bacteria/tryptophan/biological category is the most sensitive to heat (of the 6 clusters with sufficient particles for adequate statistics).

Cluster 8 is the least sensitive to heat. Some particles in the atmosphere with fluorescence spectra similar to this cluster are PAH, humic substances and HULIS. PAH typically are stable at high temperatures. Because the fraction remaining after heating varies with time, maybe the fraction of PAH in this cluster varies.

Cluster 4 is the most sensitive to heat. Tryptophan is a substituted heterocyclic aromatic compound, and is less stable than PAH.

We do not see an approach where heating might be used to reduce false positives that doesn't either decrease the count rate, or cost significantly more.

Problem With Test Particles
How do you know they are the same or have spectra similar to atmospheric particles?

Measurements we plan to do to address the above.

→Sample near sources.

Downwind from a diesel engine. Do the spectra change with distance?

Above a lawn, or in the woods. Various heights.

Near a freeway, downwind.