

Advanced Characterization of Particles and Particle-Cell Interactions



Gary Holtom, Brian Thrall, Alex Laskin, Alla Zelenyuk, Mike Alexander,
Jim Cowin

Pacific Northwest National Laboratory

Start the story with Collaboration (April 2004)
with John Storey (Oak Ridge N.L.)



Aerodyne Aerosol Mass Spectrometer (AMS)

Mike Alexander, PNNL, Doug Worsnop, Aerodyne

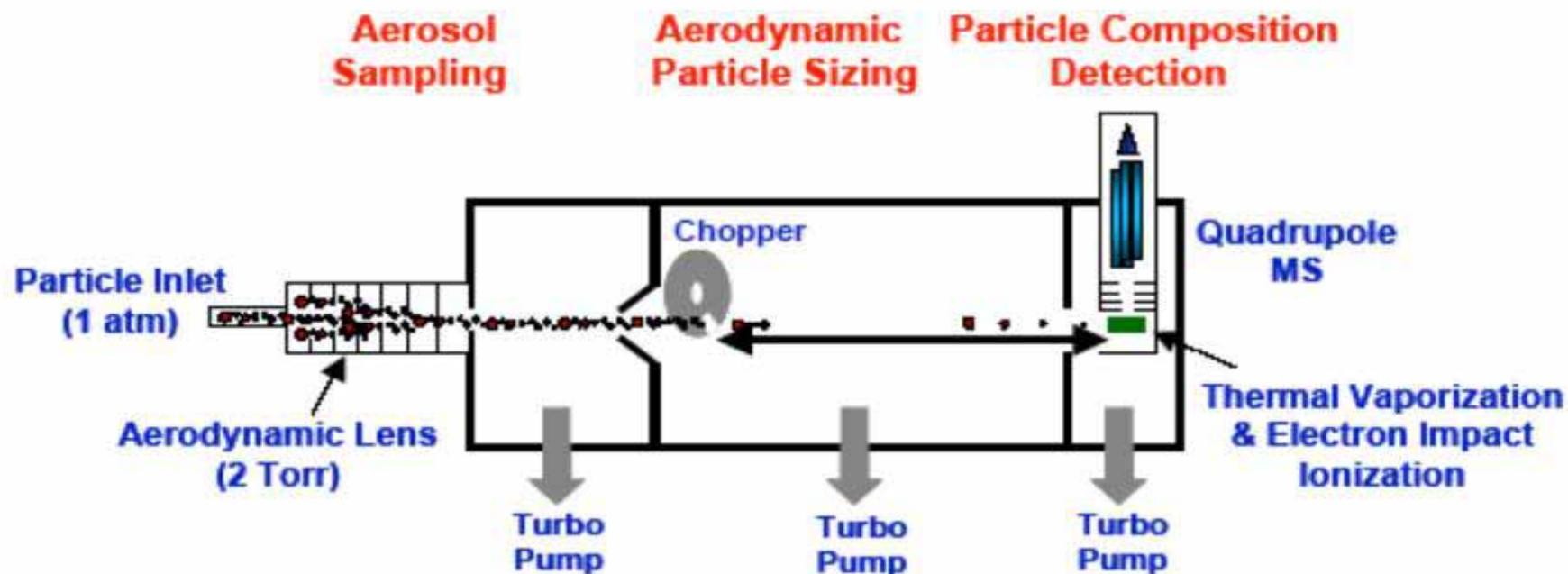
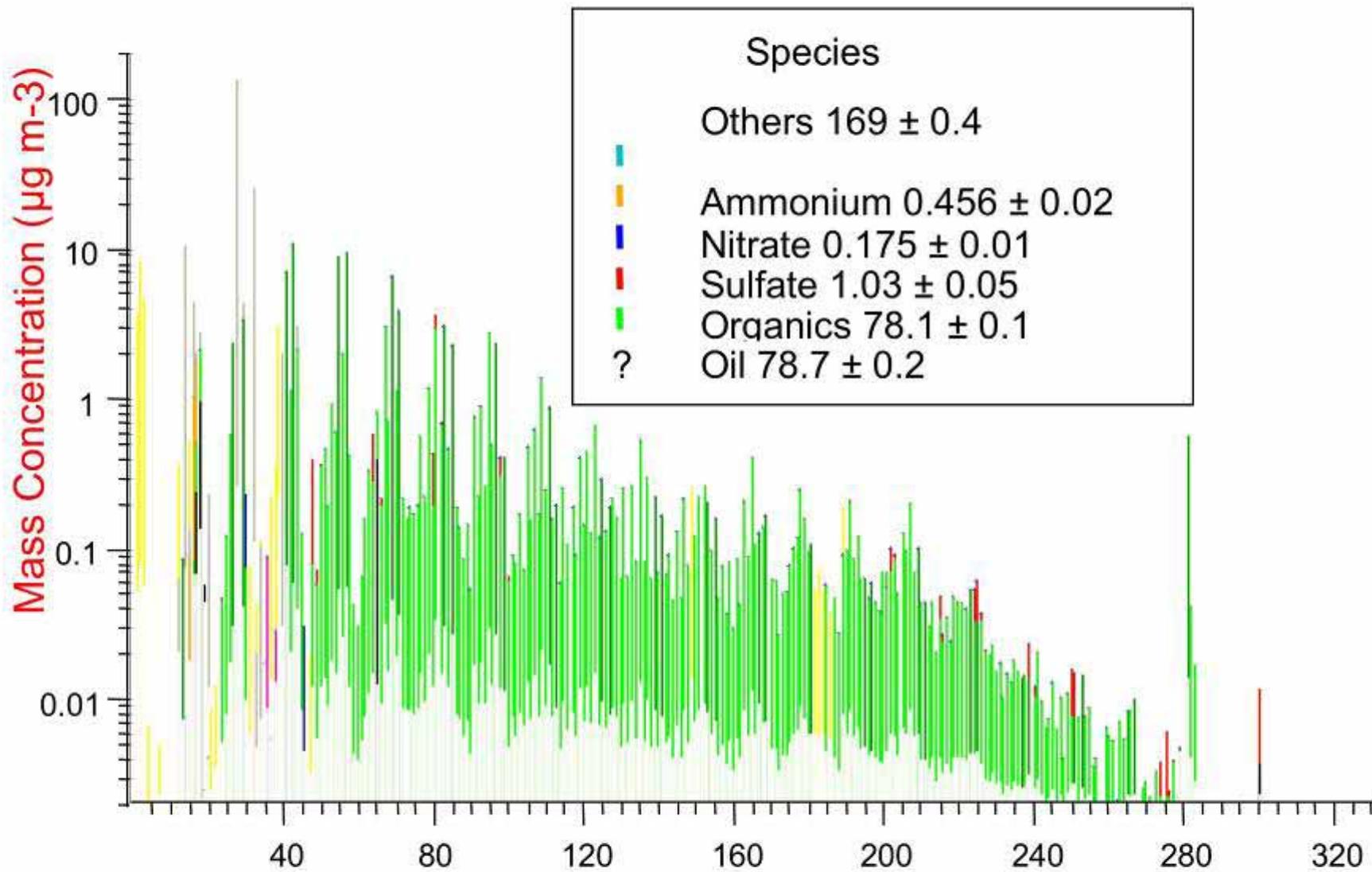


Figure 1: Diagram of AMS

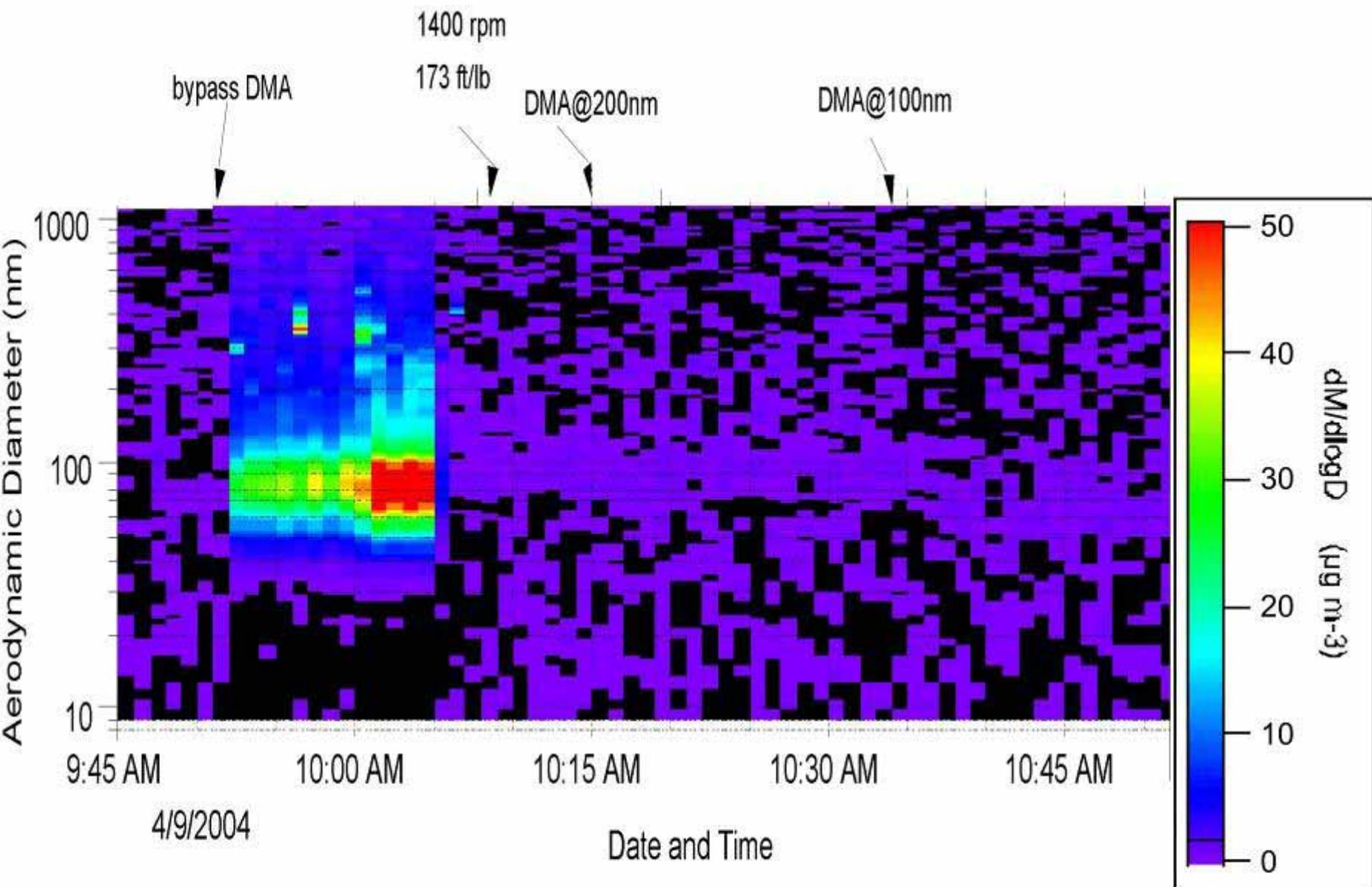
Particle Distribution, size-resolved composition, soon single particle

Quantitative for organics, semivolatiles

Truly Portable, **Fast Response for transients: 1 second**



Quantitative, Wide dynamic range



Fast enough (soon) to follow engine cycle

Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS) Alla Zelenyuk PNNL, Dan Imre

SPLAT-MS

Size, density and molecular composition of individual particles in real-time.

Aerodynamic particle lens.

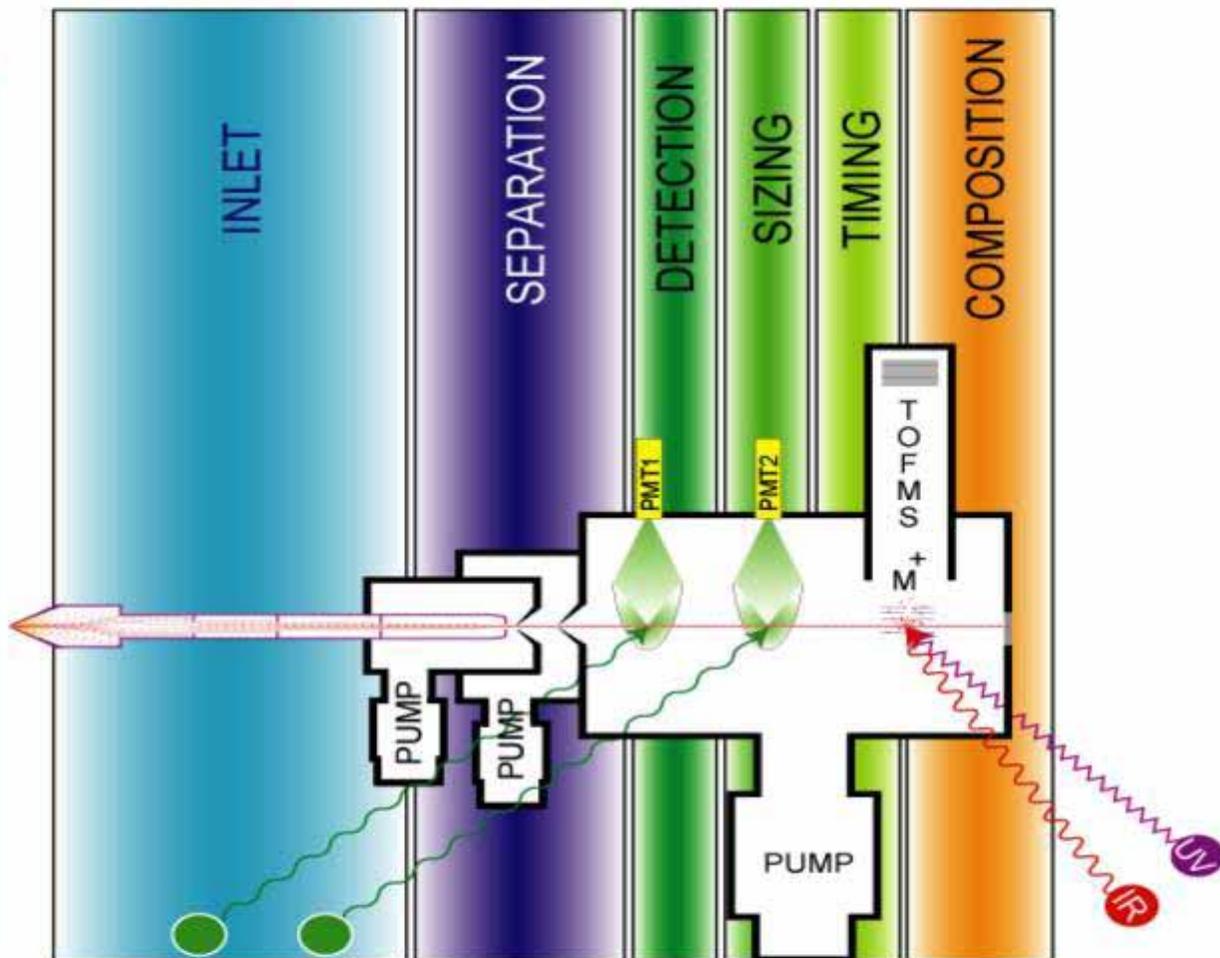
Optical detection provides particle velocity/size.

IR laser pulse evaporates particle

UV laser ionizes for TOF-MS.

20 particles/s

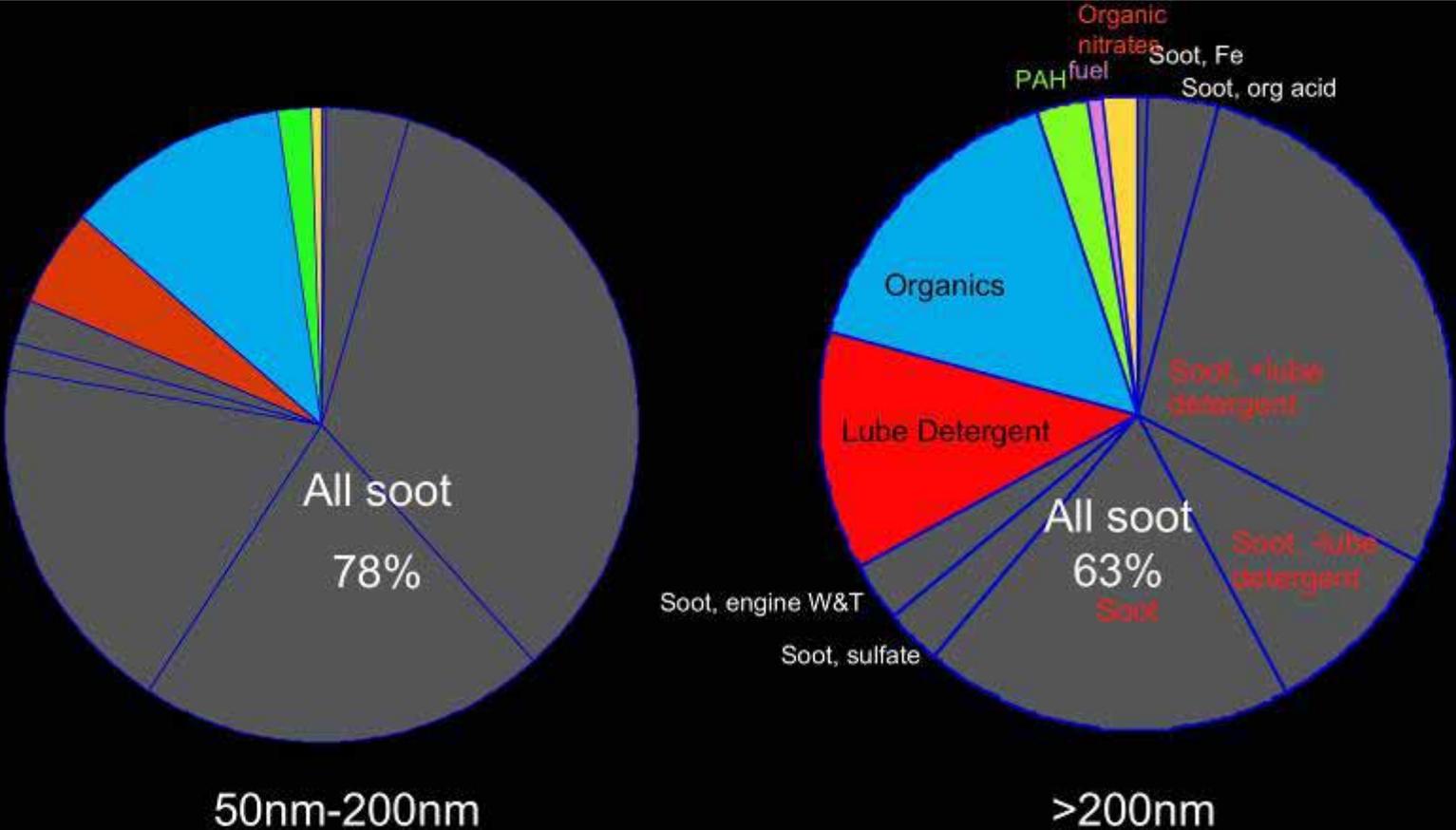
(100 in new SPLAT)



-  Green laser for detection
-  Infra Red laser for evaporation
-  UV laser for ionization

Single Particle Size and Composition Measurements

Cluster Analysis to identify particle groups



Preliminary analysis of data obtained from *Off-road industrial vehicle engine*

Diesel soot density and fractal dimension

Aerodynamic size depends on geometry and mass (density)

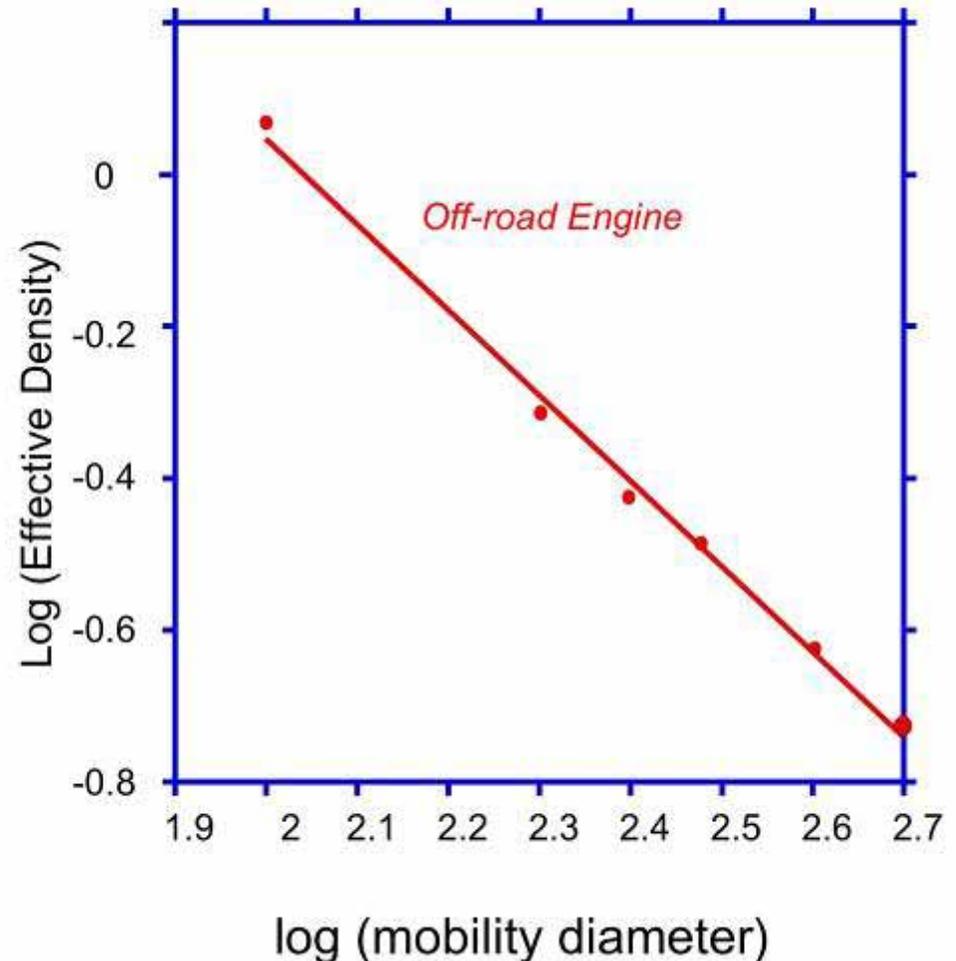
Mobility size depends only on geometry

$$\text{Density} = D_{\text{aero}}/D_m$$

$$\text{Density} = C D_m^{D_f-3}$$

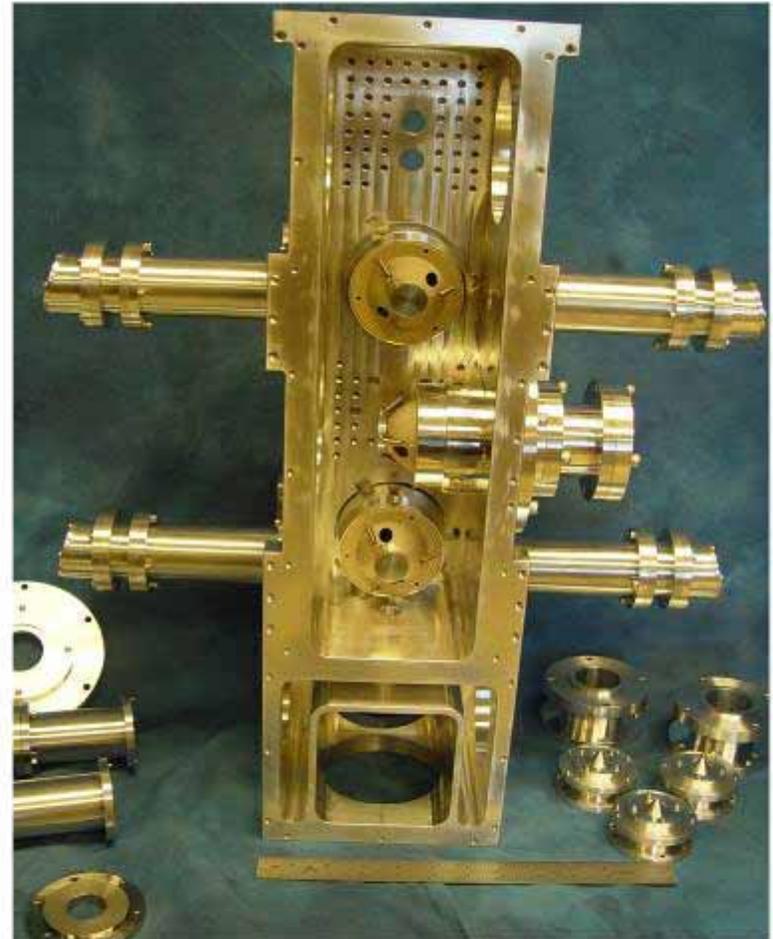
$$D_f = 1.87$$

Consistent with fractal dimension for diffusion-limited cluster-cluster agglomeration

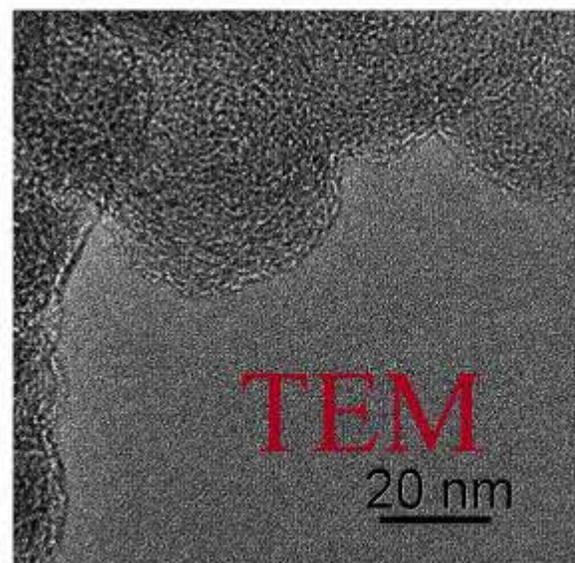
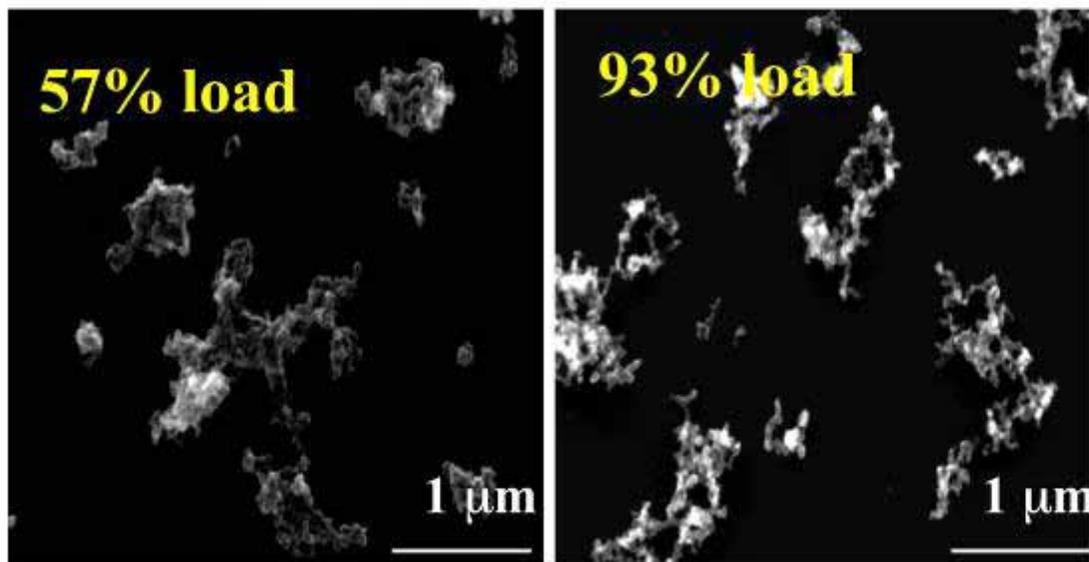
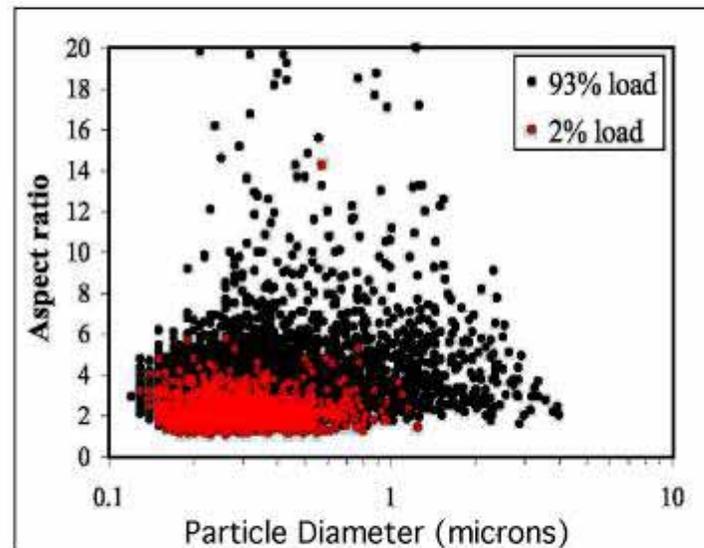
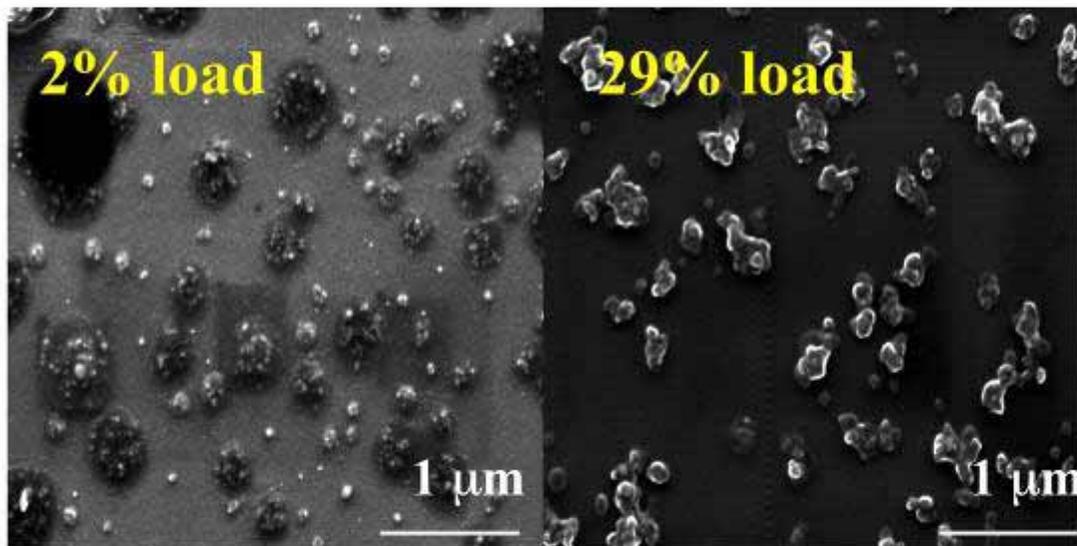


**NEW SPLAT: Small, portable, better:
Size, composition, shape, density, soot content, and
hygroscopicity of individual particles**

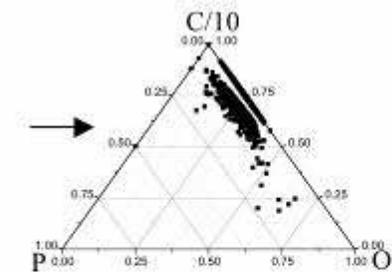
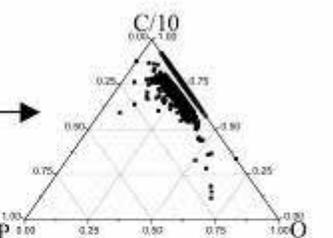
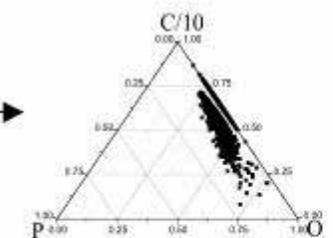
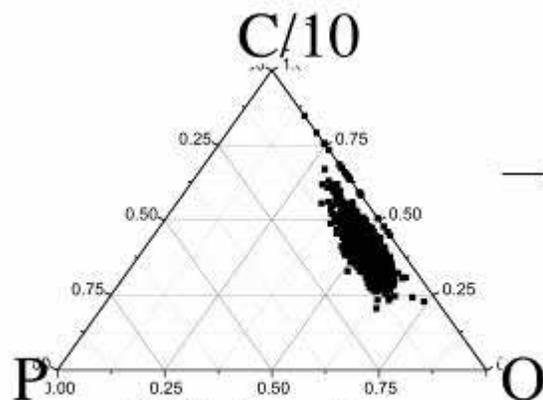
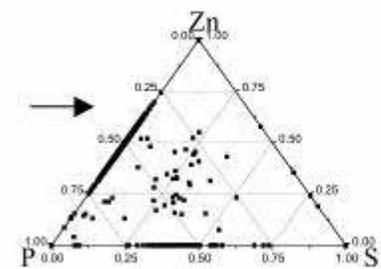
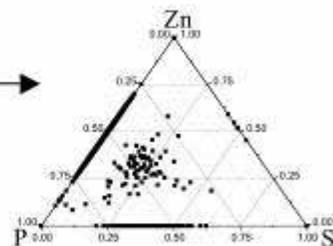
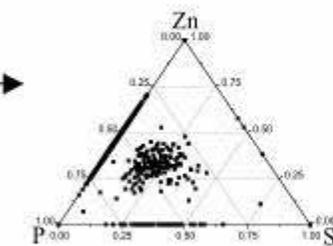
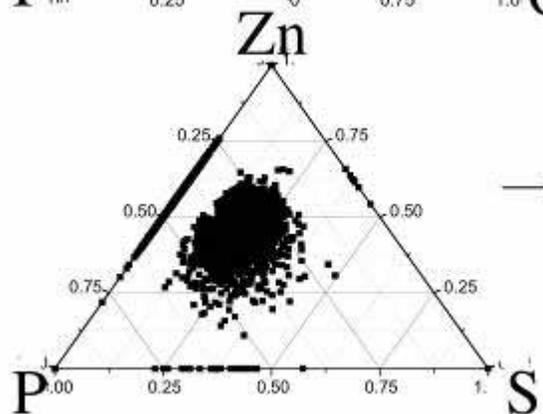
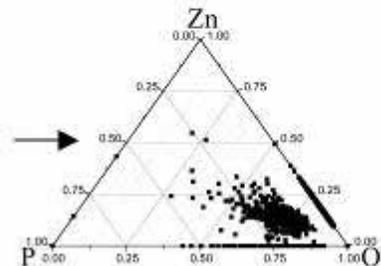
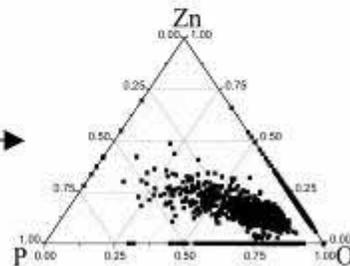
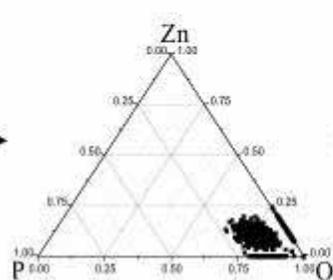
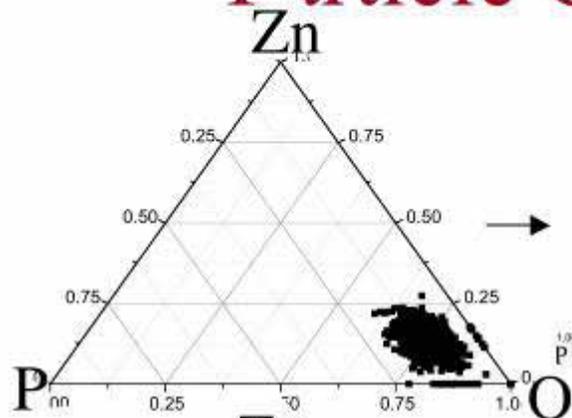
- Size range –
40 nm to 3 micron
- Rate – 100 particles/sec
- Composition – IR/UV
- Shape – light scattering
- Soot Content – Laser-induced
incandescence



Particle Morphology Changes (SEM)



Particle Composition (CCSEM/EDX)



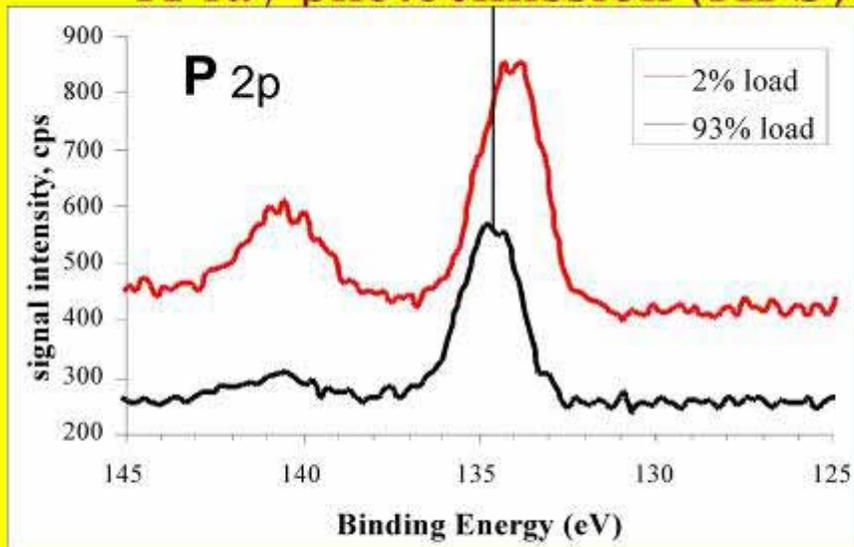
29% load

57% load

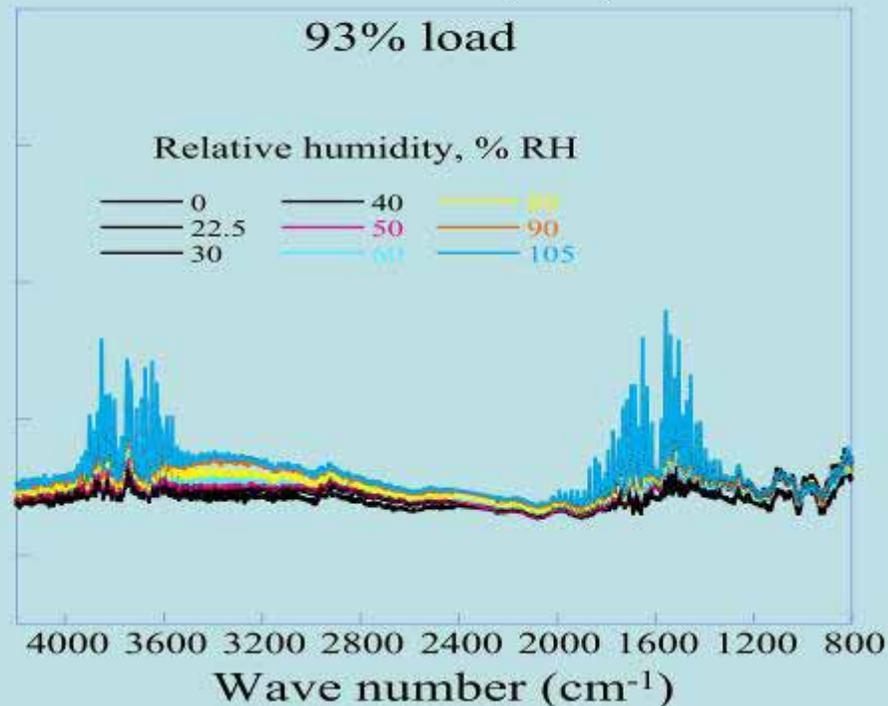
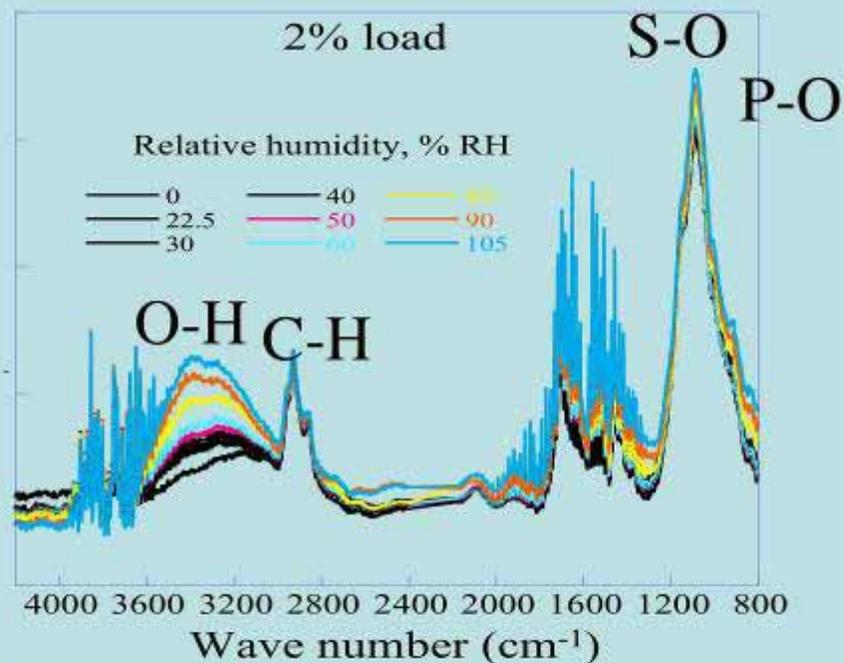
93% load

2% load

X-ray photoemission (XPS)



FTIR Microscopy: Hygroscopic properties of exhaust particles vs engine load

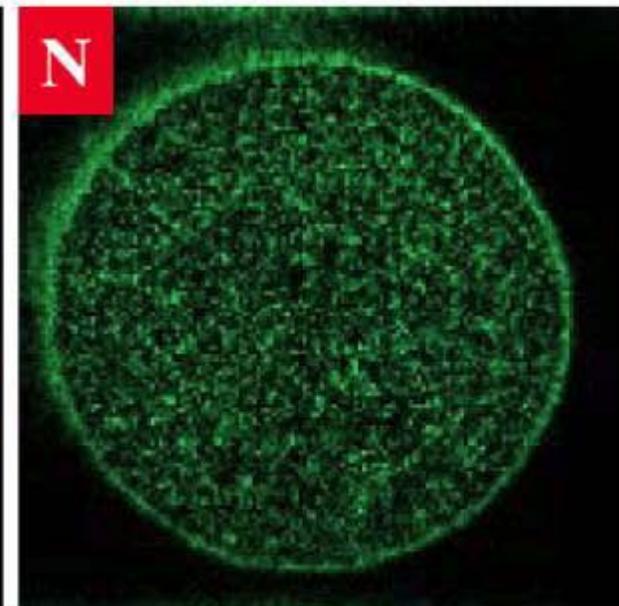
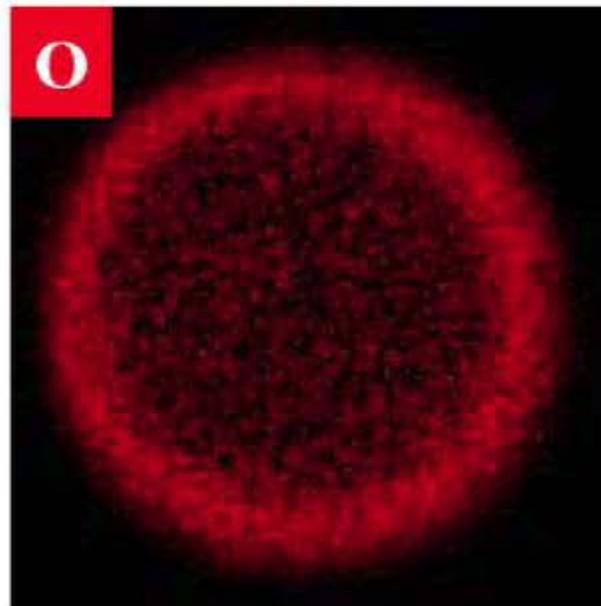
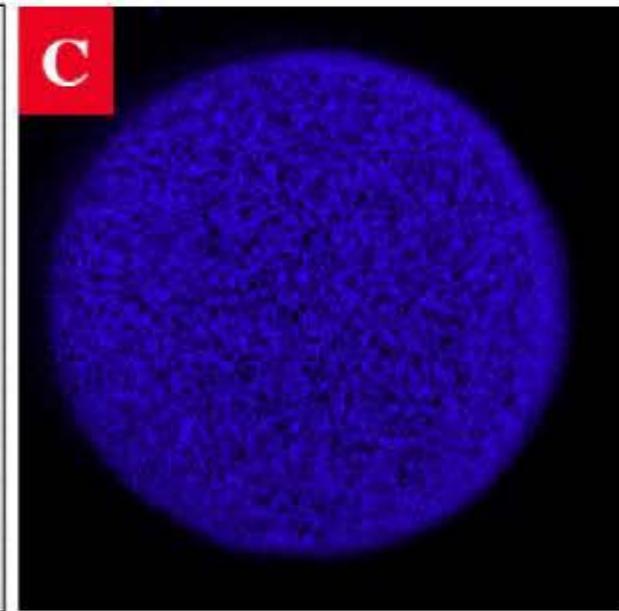
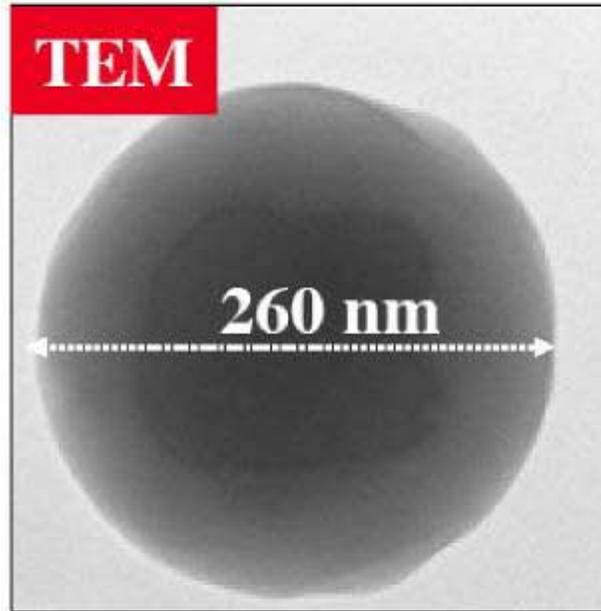


Atmospheric Aging Of Particles

What is emitted
changes radically in
the atmosphere

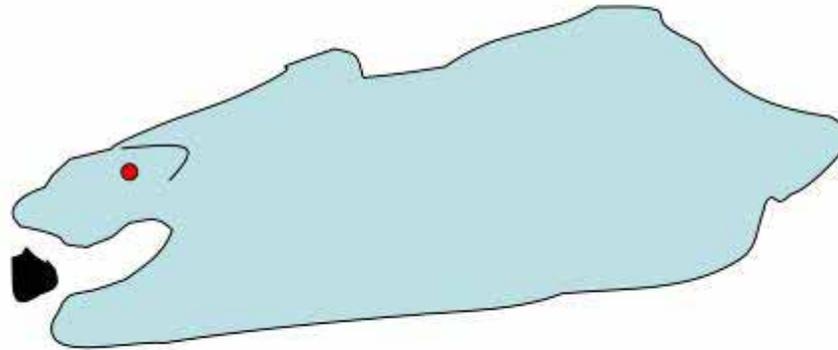
Attack by OH radicals
 NO_3 , HNO_3 ,
 H_2SO_4 , H_2O_2 ,
Halogen atoms,...

Nitration
Bromination
Peroxides/epoxides
Hypochlorites



We need **Rapid Screening** means to quantify **Health effects of Particles**

B-Y Chin, G Holtom and Brian Thrall



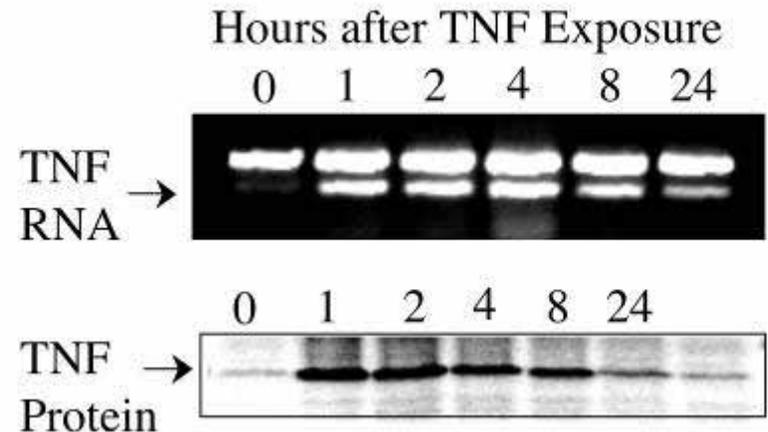
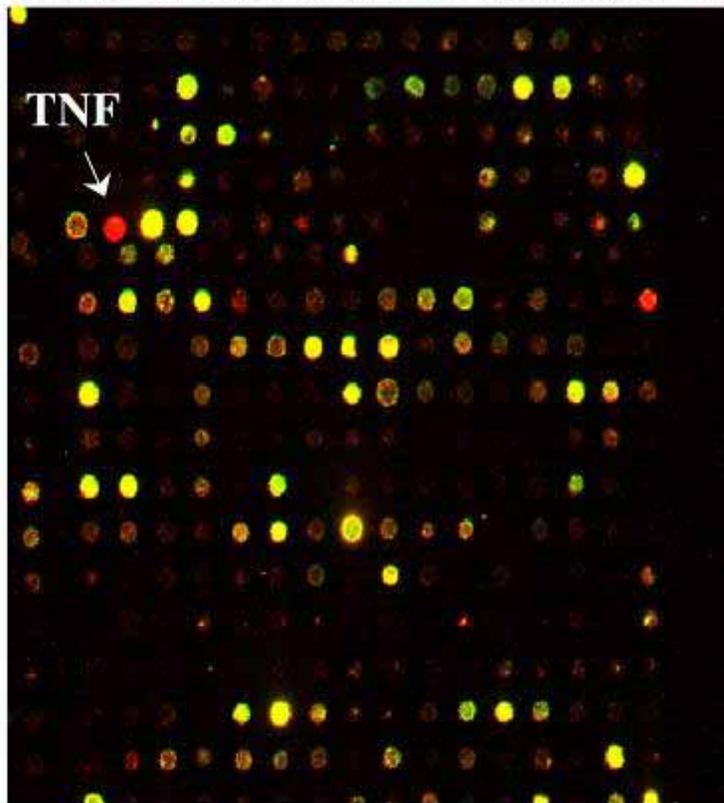
Macrophages roam the lung, to eat up particles.
If they get/cause inflammation, this is bad.

Tumor Necrosis Factor (TNF) response of PM-exposed macrophages
starts before and persists long after cells eat the PM...

What determines the persistence of the inflammatory response?

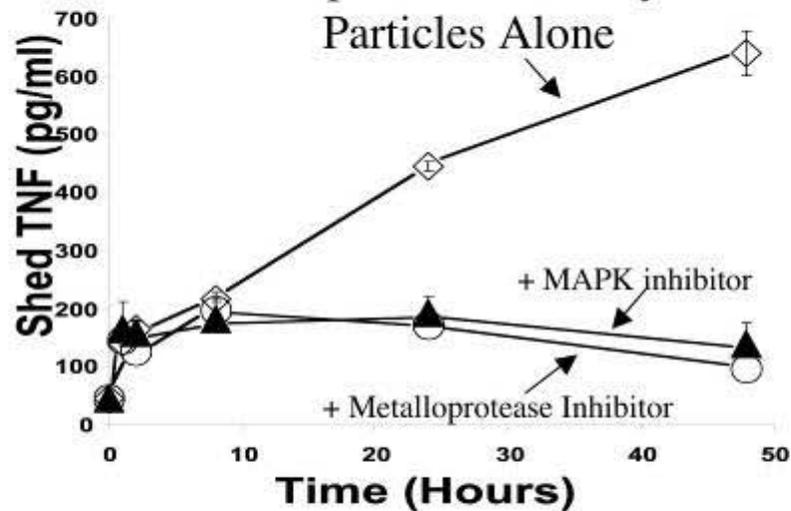
RNA expressed tells what proteins are being commanded to activate 0, 1, 2,.... hours after PM exposure

Microarray Studies in Macrophages
Reveal TNF Induces Its Own Expression (1 Hr)



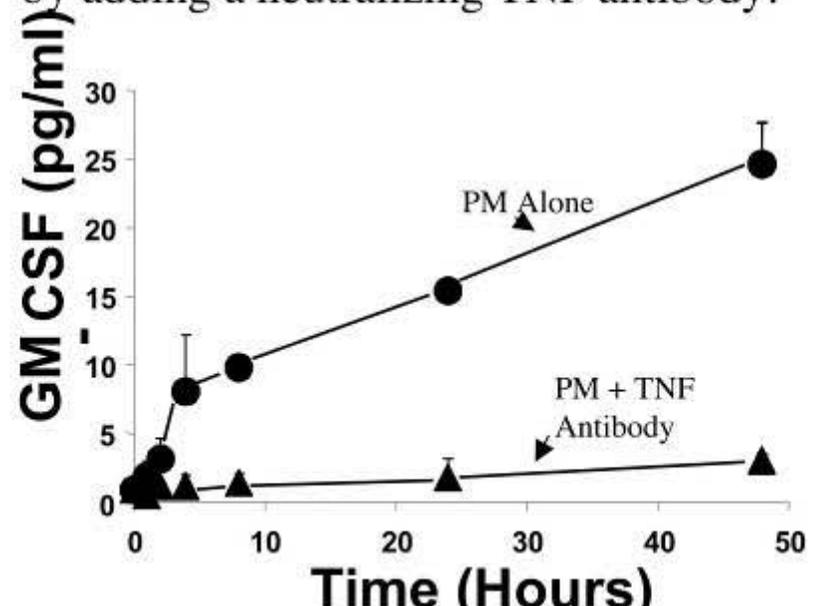
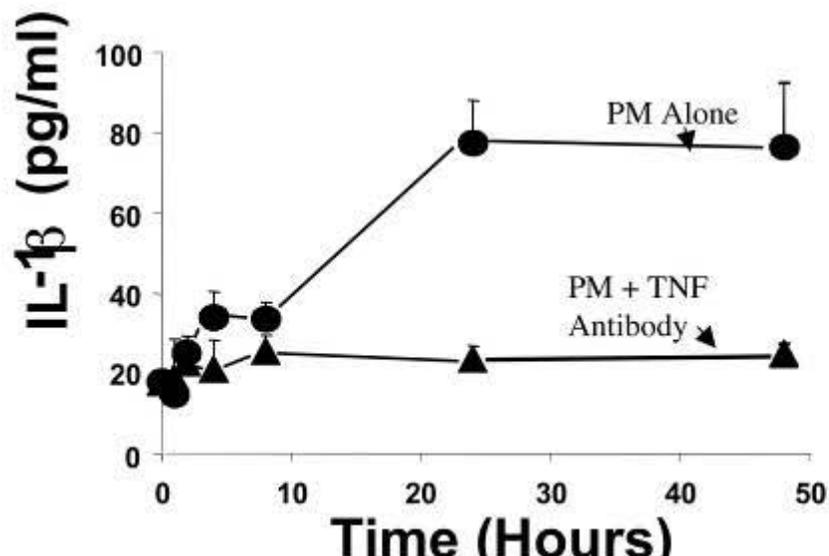
End result: Amplification of TNF Signaling Pathways Associated with Inflammation?

Driven by Sustained Activity of MAPK and Metalloprotease Pathways



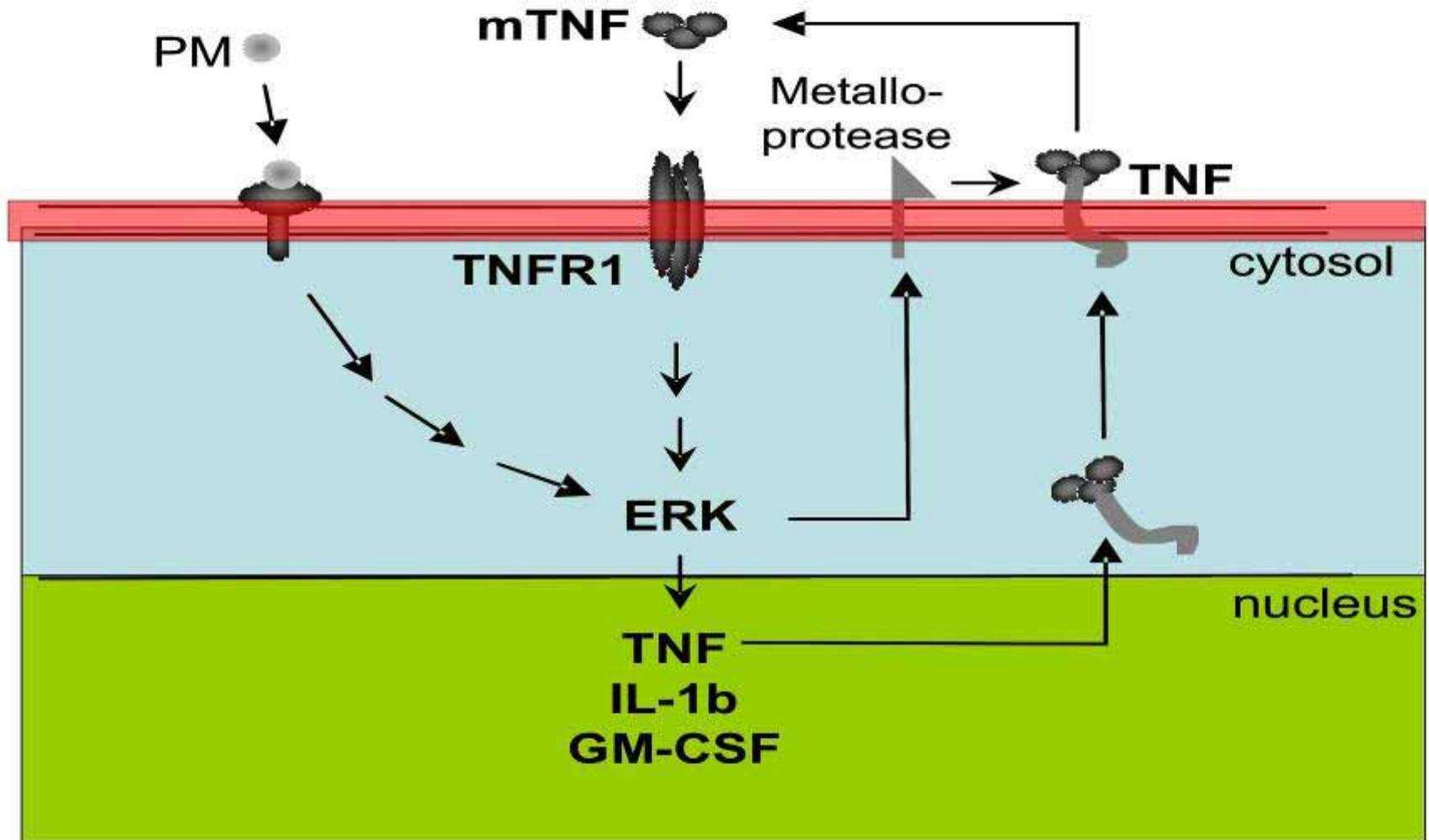
Extracellular TNF Released by PM-Activated Macrophages Causes Induction of Other Pro-inflammatory Cytokines

Synthesis and release of the cytokines IL-1 β and GM-CSF are markedly reduced when extracellular TNF is “sequestered” by adding a neutralizing TNF antibody.



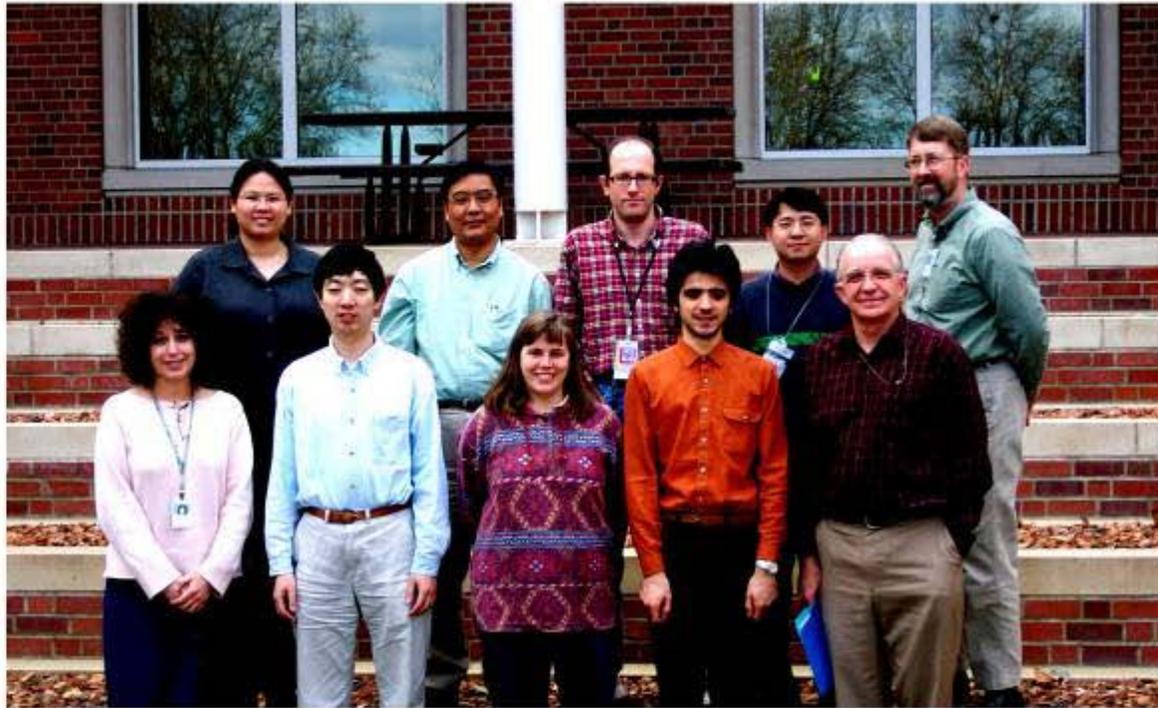
Positive Feedback Loops Involved in TNF Signaling

Determine the Persistence of the Macrophage Inflammatory Response



Chin, BY, Holtom, GR, and BD Thrall (submitted).

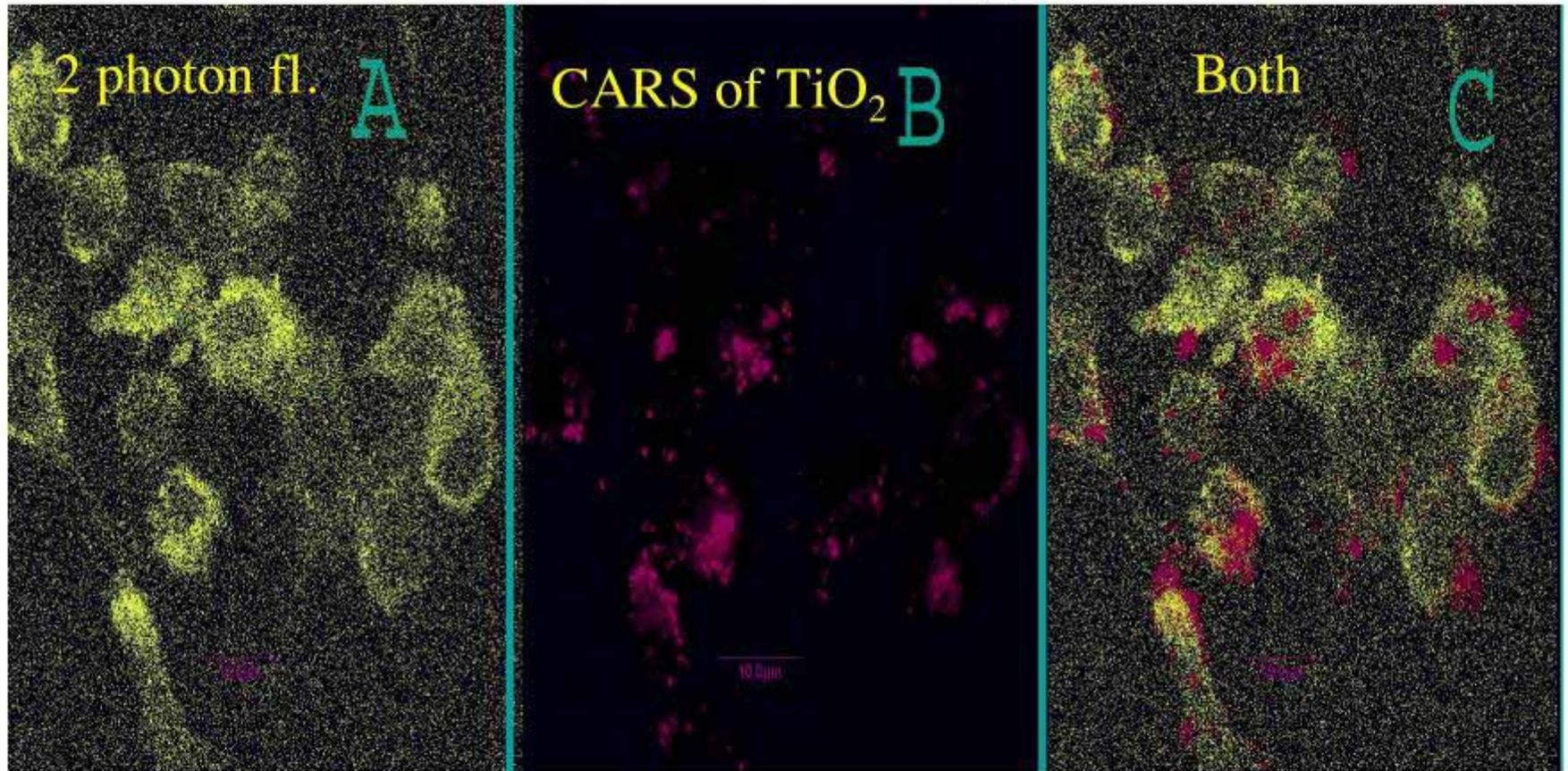
Where do nanoparticles go in cells? CARS and linear and non-linear fluorescence microscopy



Gary Holtom, Yuangang Zheng, and Steven Colson

The cellular observatory team

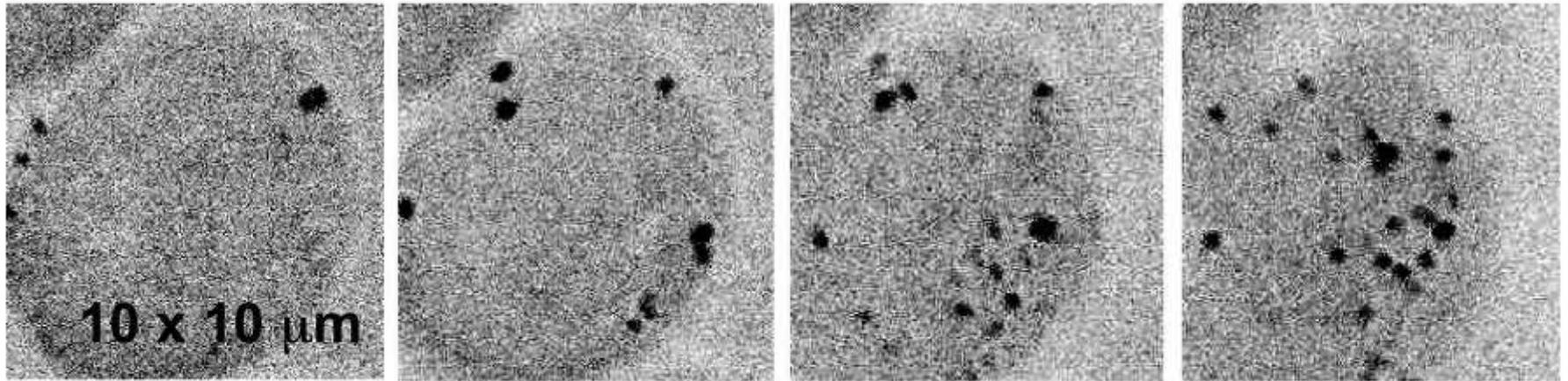
3-D CARS image of macrophages that devoured TiO_2 Particles



Imaging non-fluorescent titanium dioxide nanoparticles *in vitro* by nonlinear optical microscopy

Y Zheng, B-Y Chin, B Thrall S Colson and G Holtom (submitted)

3-D CARS image of iron oxide nanoparticles



Macrophage RAW264.7 at 2200 cm^{-1} four consecutive slices

$1 \mu\text{m}$ spacing

Macrophages in carbon black suspension

CARS at 1400 cm^{-1}

$70 \times 70\ \mu\text{m}$

Two-photon fluorescence

