Perspectives on Research Needs for Ultrafine Particulate Matter (PM)

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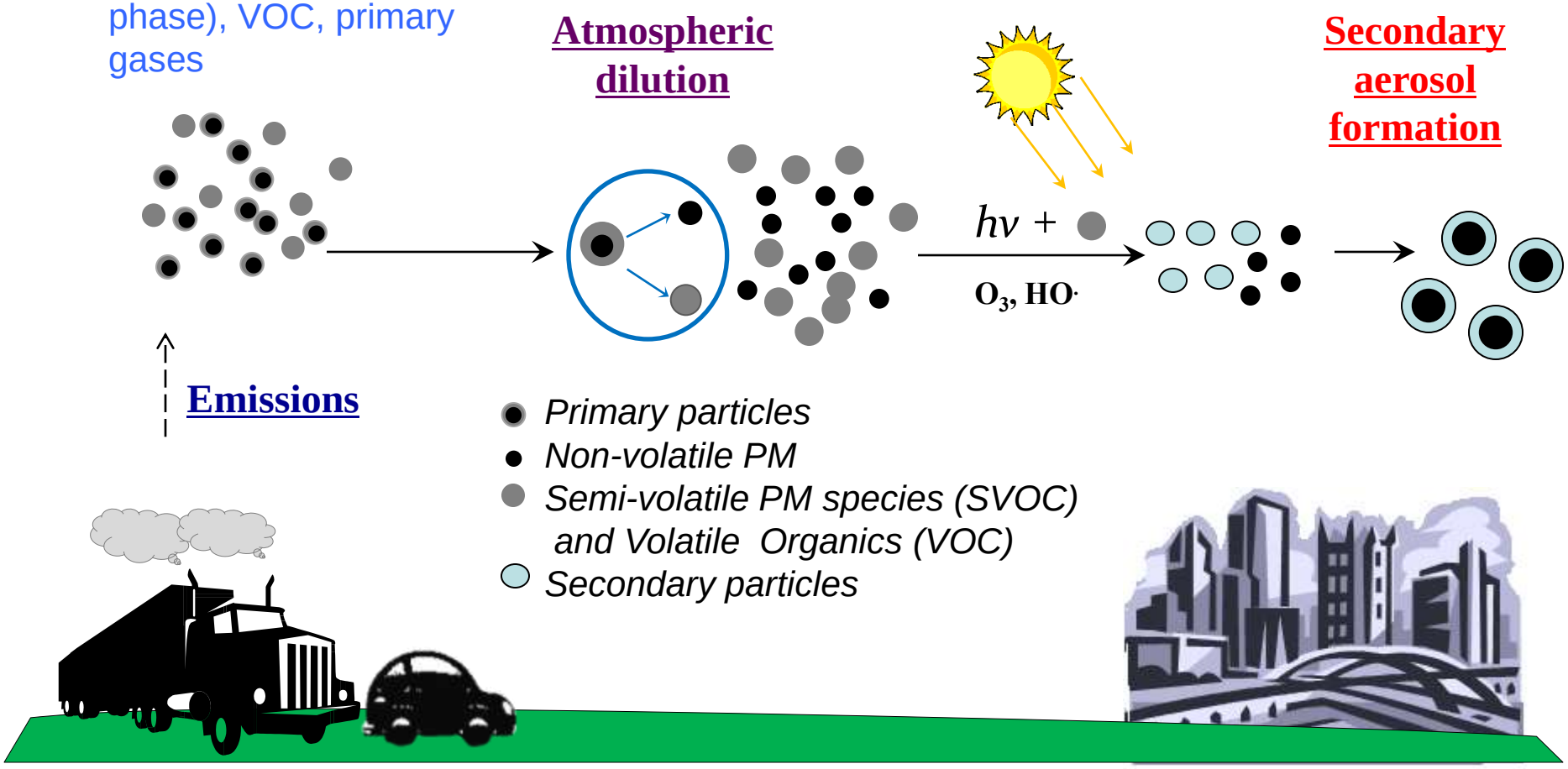
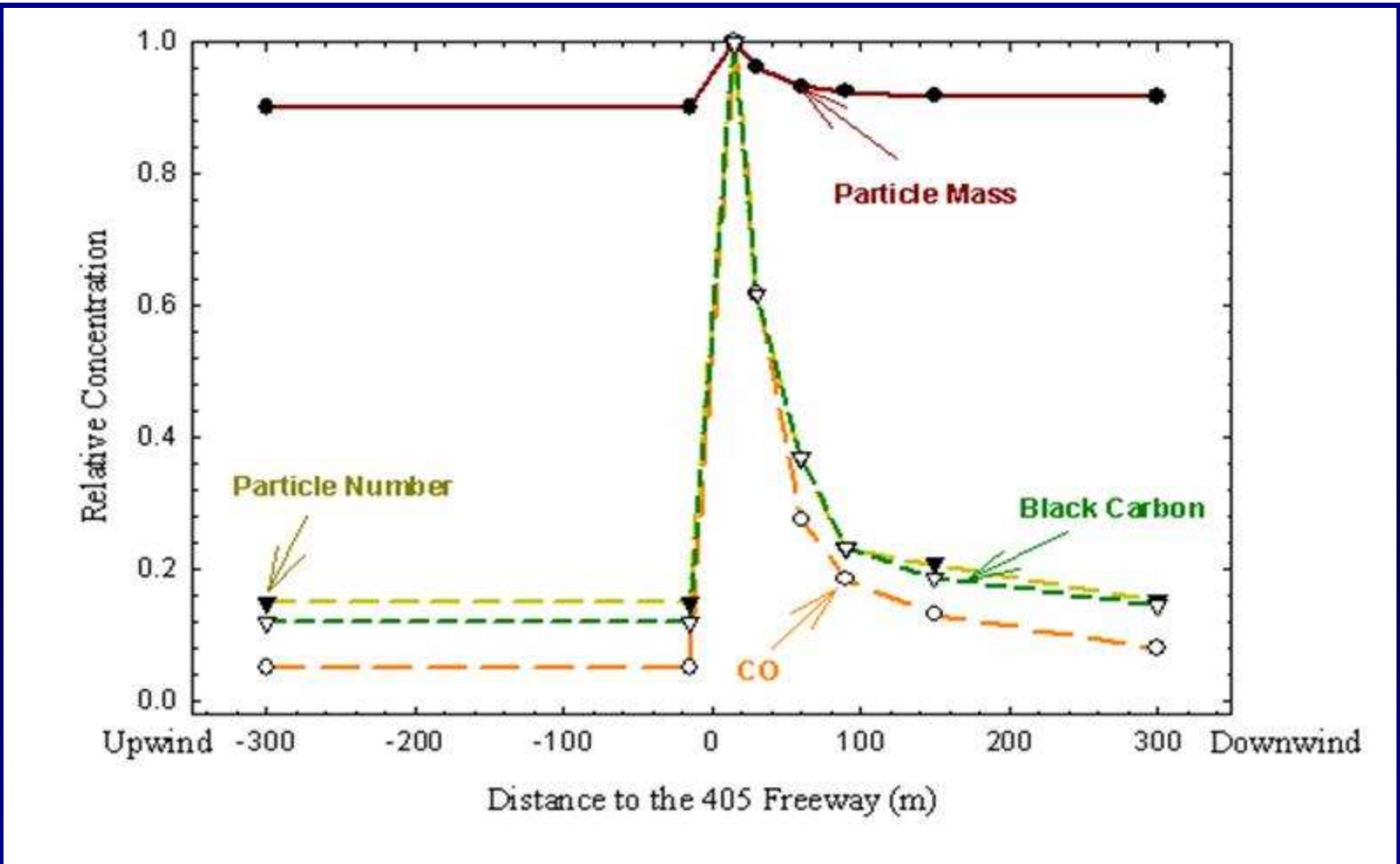
1. **Emission Sources of Air Pollutants**
- **Traffic, Freeways, Ports, Power plants**
- Freshly emitted mixture of non-volatile PM, SVOC (PM and vapor phase), VOC, primary gases

2. Atmospheric Dilution
- Phase transformation
- Volatilization of primary SVOC and partitioning from PM phase into gas phase

3. Atmospheric Aging and Photo-Chemical Reactions
- Photo-chemical reactions of gas phase SVOC with O3 and oxidant gases
- Formation of Secondary Organic Aerosol(SOA)



Decrease in Concentration of PM with Distance from Freeway higher for smaller particles due to dilution + volatilization (Zhu et al, Atmos Environ. 2001)



Due to their semi volatile nature, UFP are operationally defined- they represent super saturated vapors condensing during cooling of the exhaust

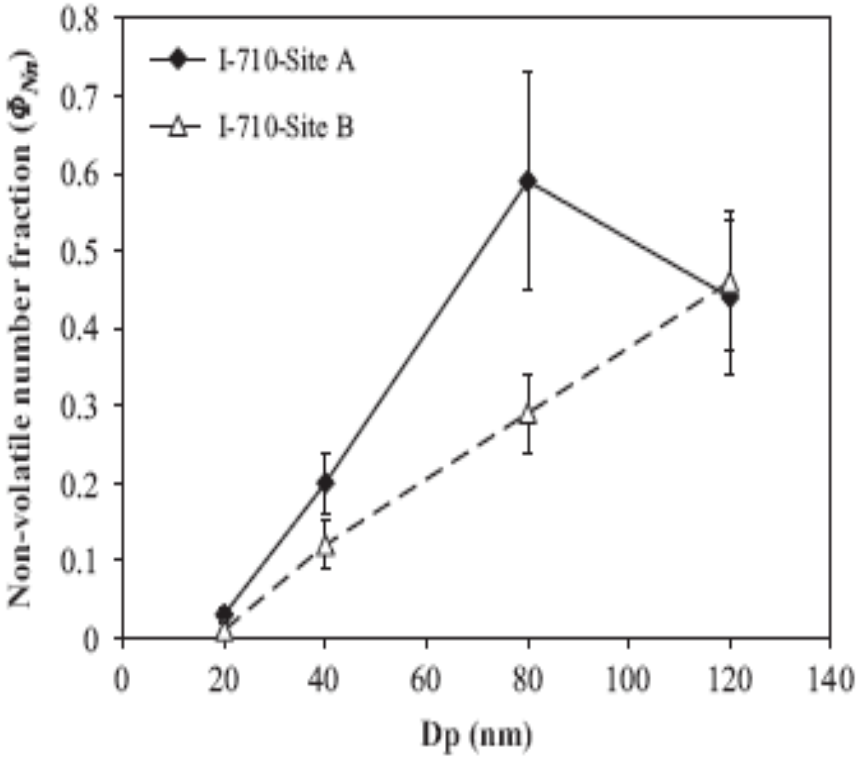
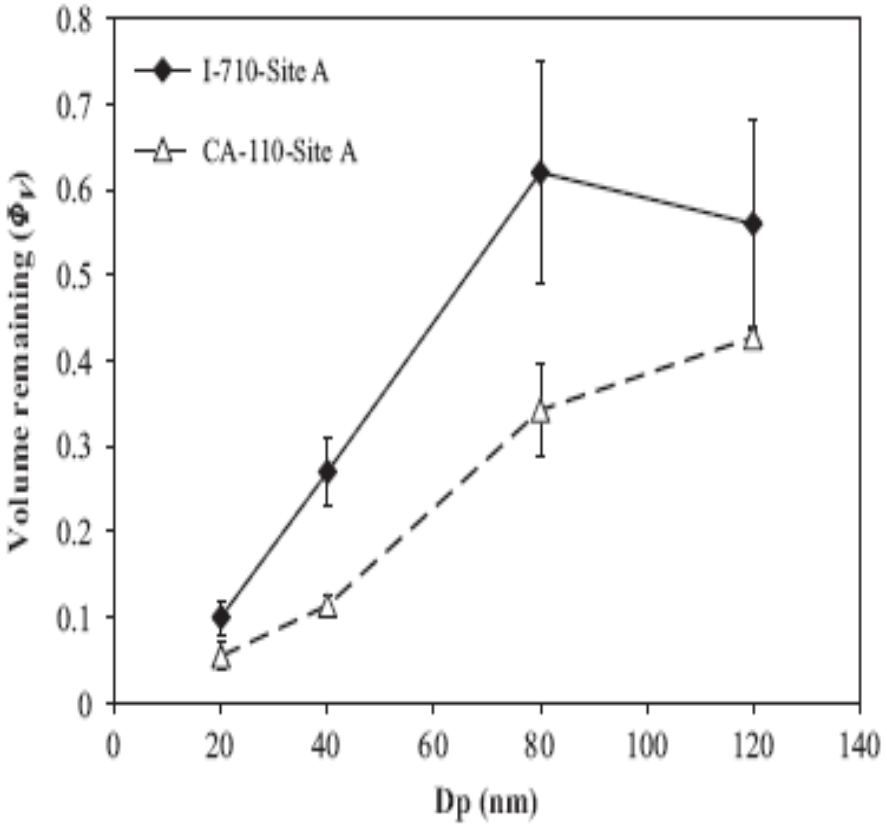


Fig. 5. Non-volatile number fraction at site A and site B.

Number and Volume of PM remaining after heating at the CA-110 and the I-710



- Diesel particles in general less volatile than gasoline
- Smaller particles in the UF range are the most volatile

PM Emissions from Newer Technologies

4 vehicles, 7 configurations, 3 driving cycles

Vehicle

Veh#1

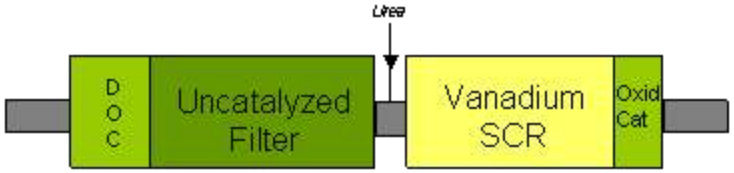
1998 Cummins Diesel
11L, 360,000 miles,
BASELINE VEHICLE

After-treatment

NA

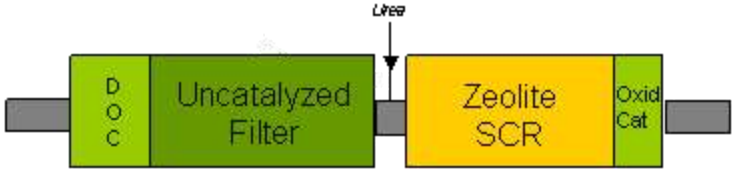
50,000 mi

CRT®



50,000 mi **50,000 mi**

V-SCRT®*



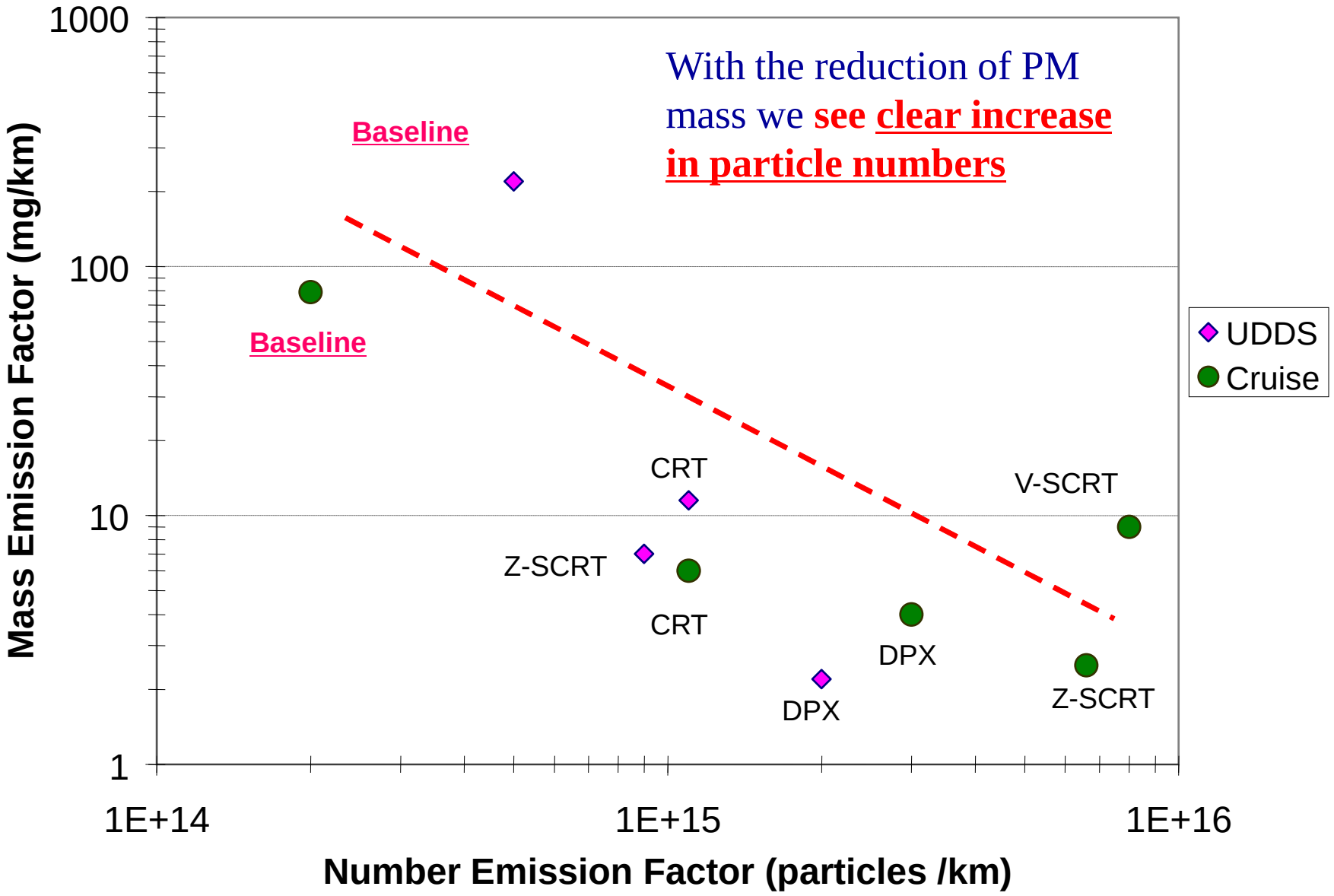
50,000 mi **0 mi**

Z-SCRT®*

Abbreviation Baseline

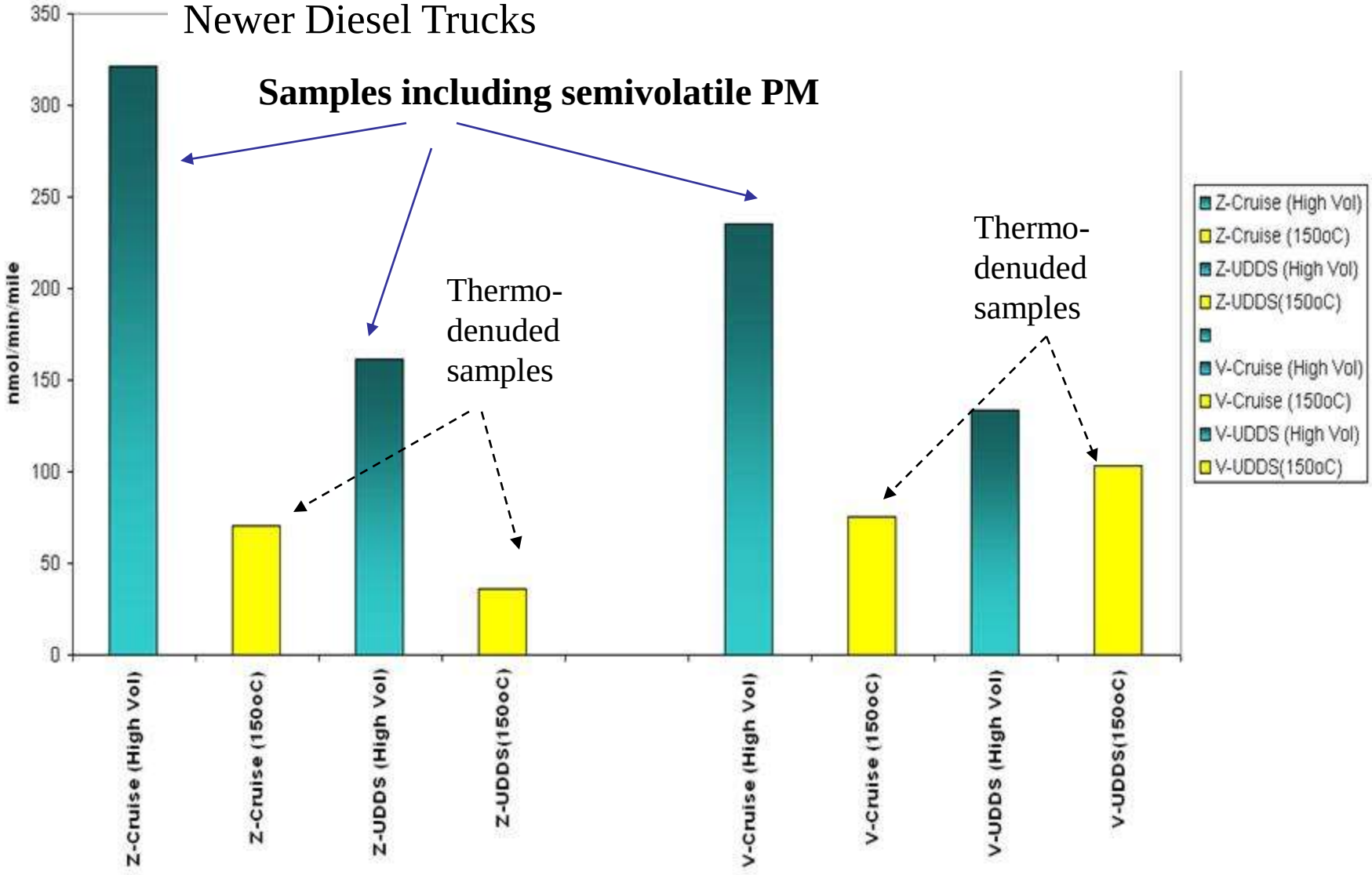
- **SCRT® systems used in this project are development prototypes, not commercial units.** **Biswas et al ES&T 2009**

Number vs Mass Emission Factors (EF) from Older and Newer Diesel Trucks

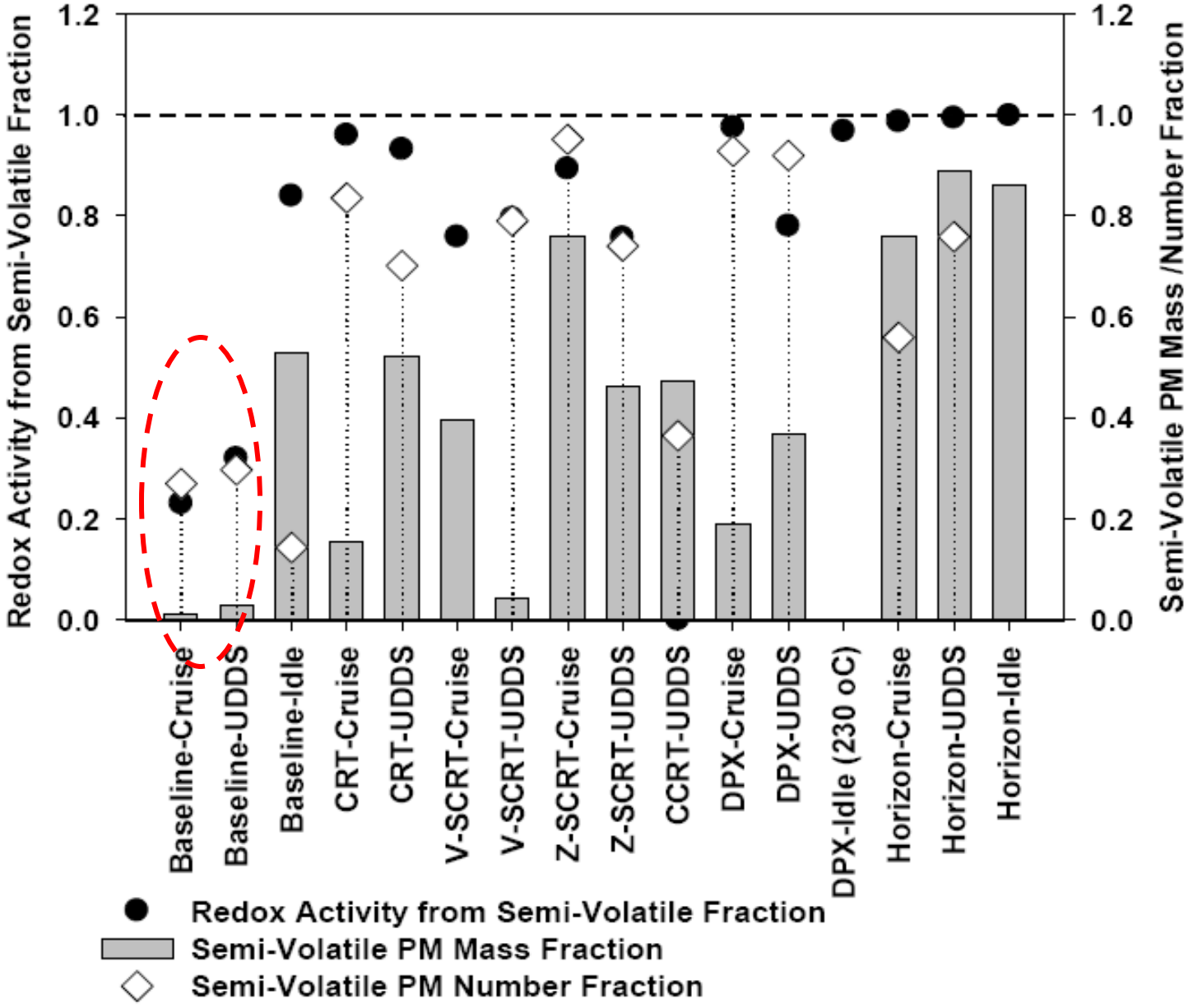


Biswas et al. Atmos. Environ, 2008

Redox Activity (DTT assay) of Semivolatile and Total PM from Newer Diesel Trucks

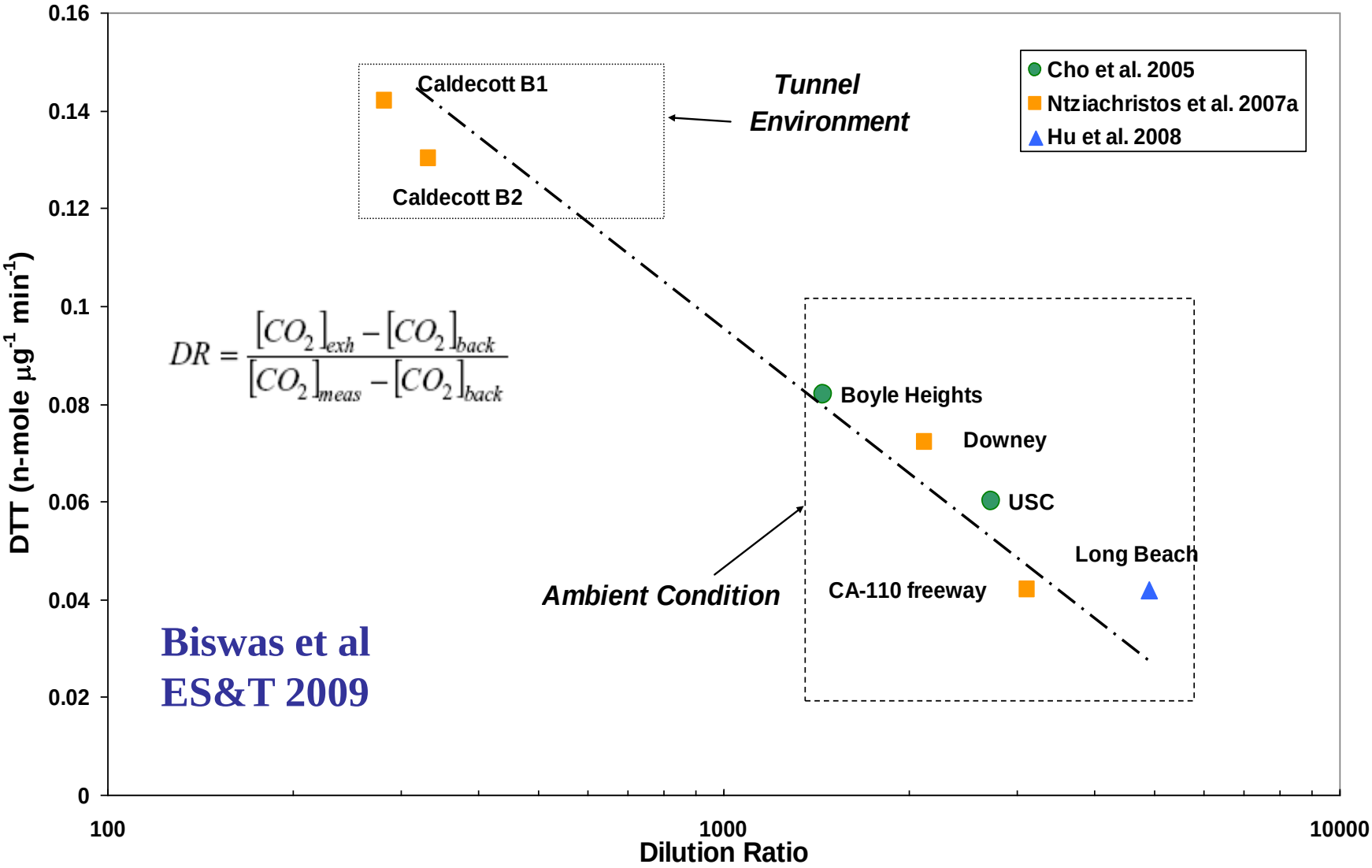


DTT rate of consumption per PM mass (nmoles/μg PM/min) is **much higher when the semi-volatile fraction is included**

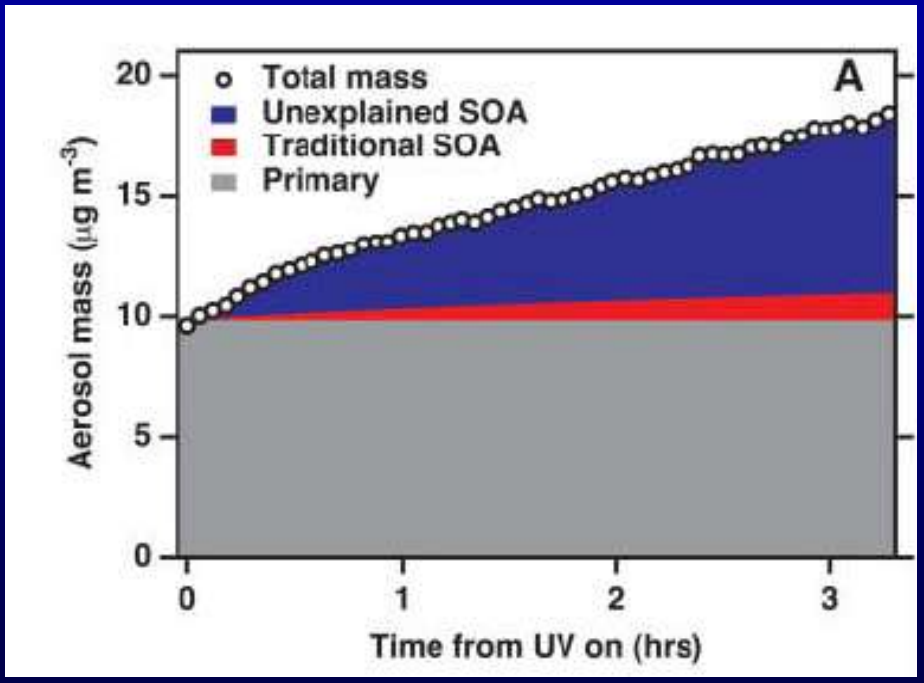


Semi-volatile PM faction accounts for over 80- 90% of the per PM mass toxicity (Biswas et al, ES&T, 2009)

Redox Activity per PM Mass Decreases with Atmospheric Dilution

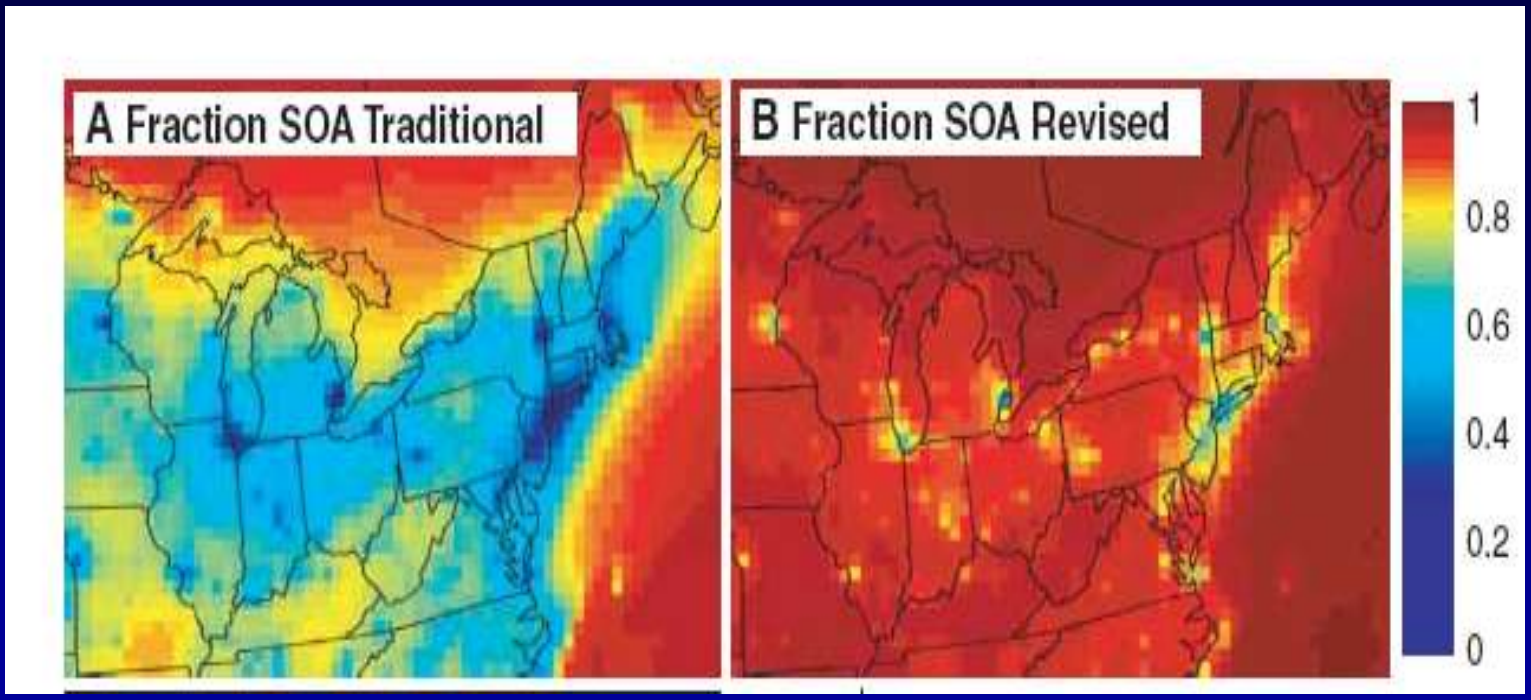


- Dilution ratio affects PM content of semi-volatile species
- Redox activity (DTT consumption) decreases with higher dilution
- Semi-volatile fraction are more redox active



Robinson et al. [Science 2007]

- Oxidation of primary diesel exhaust
- Secondary Organic Aerosol (SOA) from Traditional gas phase precursors accounts only for 15-20% of total measured SOA
- The rest is a result of oxidation of semivolatile organic species (SVOC)



Revised model taking into account SVOC oxidation increases overall SOA/POA ratio in urban areas

Versatile Aerosol Concentration Enrichment System (VACES)

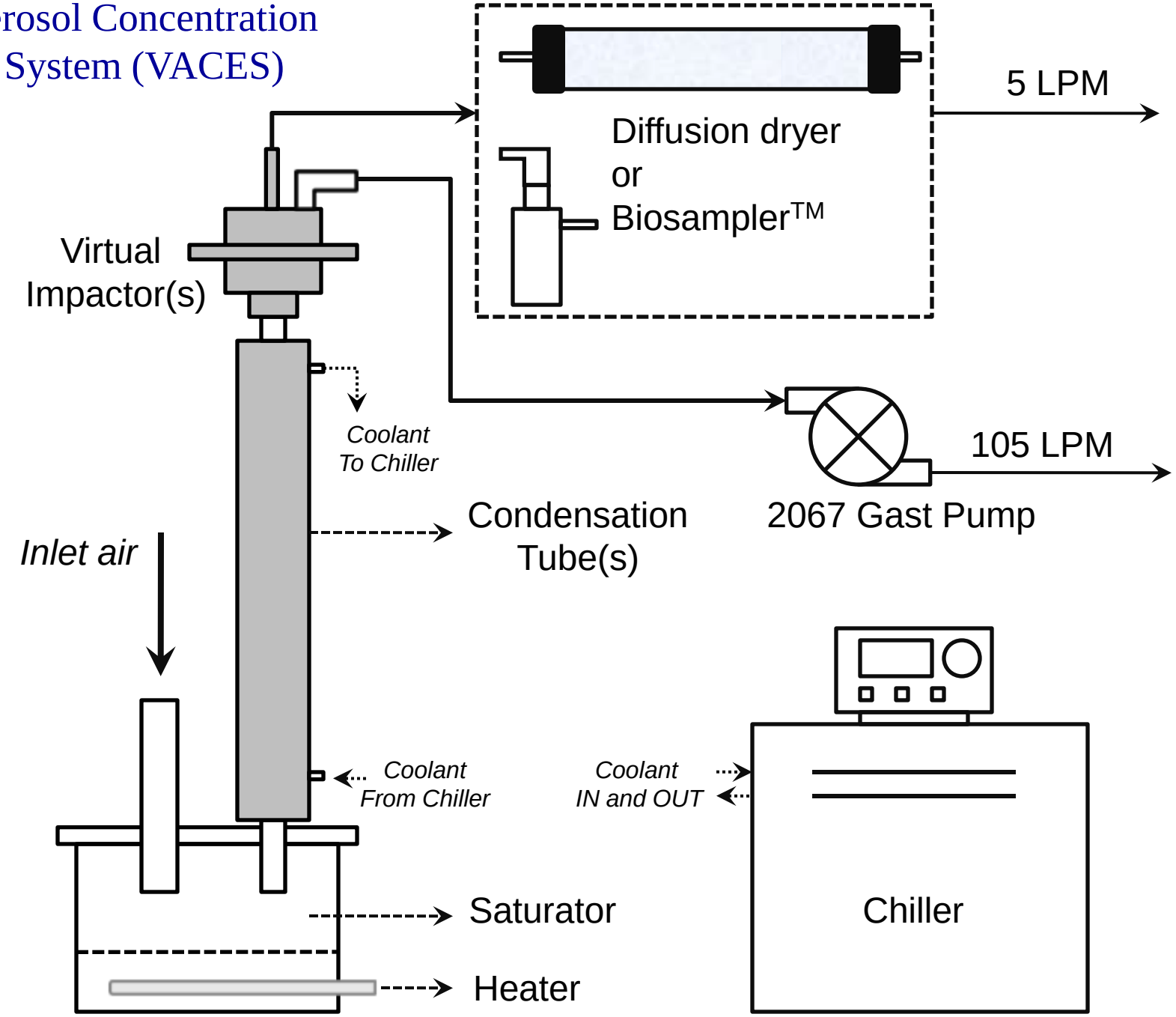
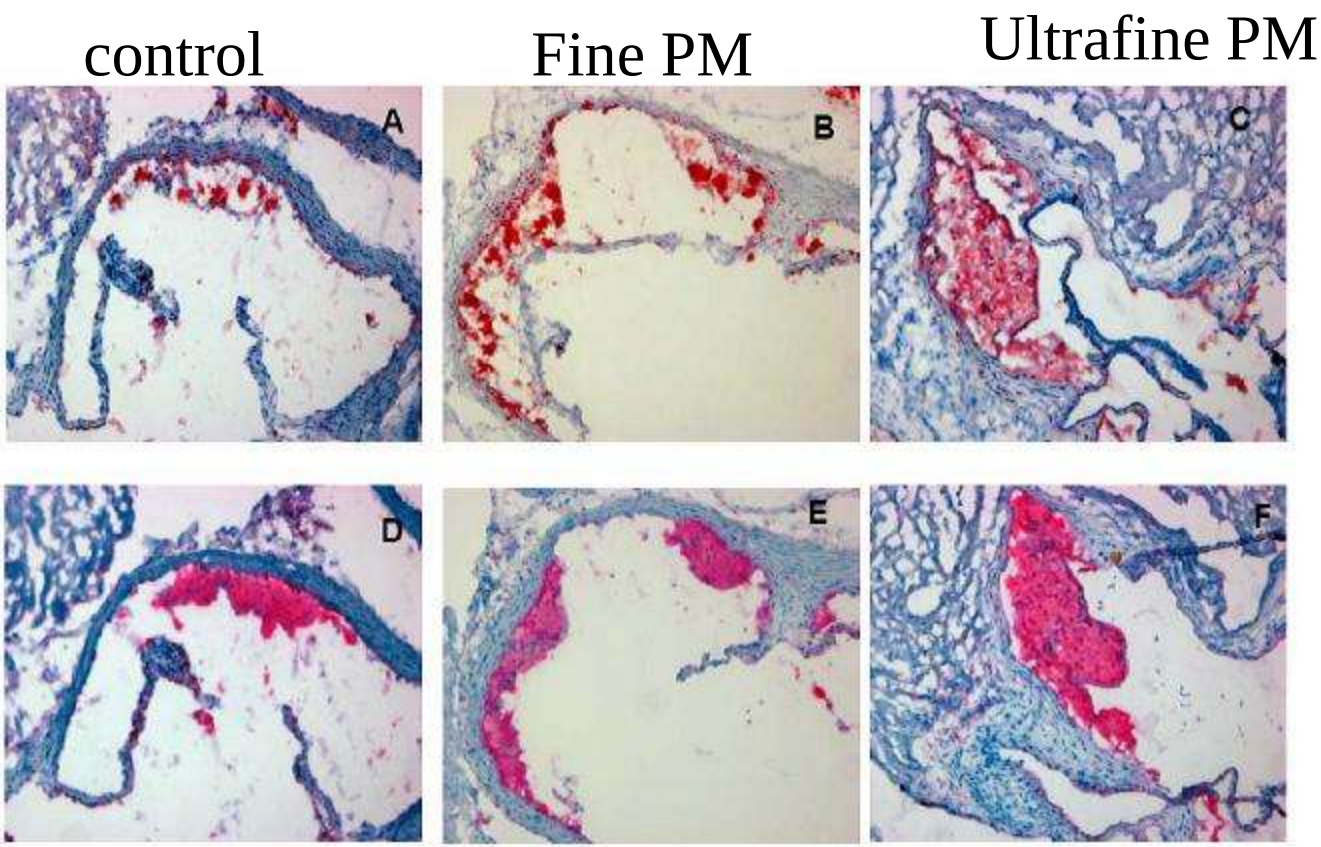


Figure 2. Representative histological photomicrographs.

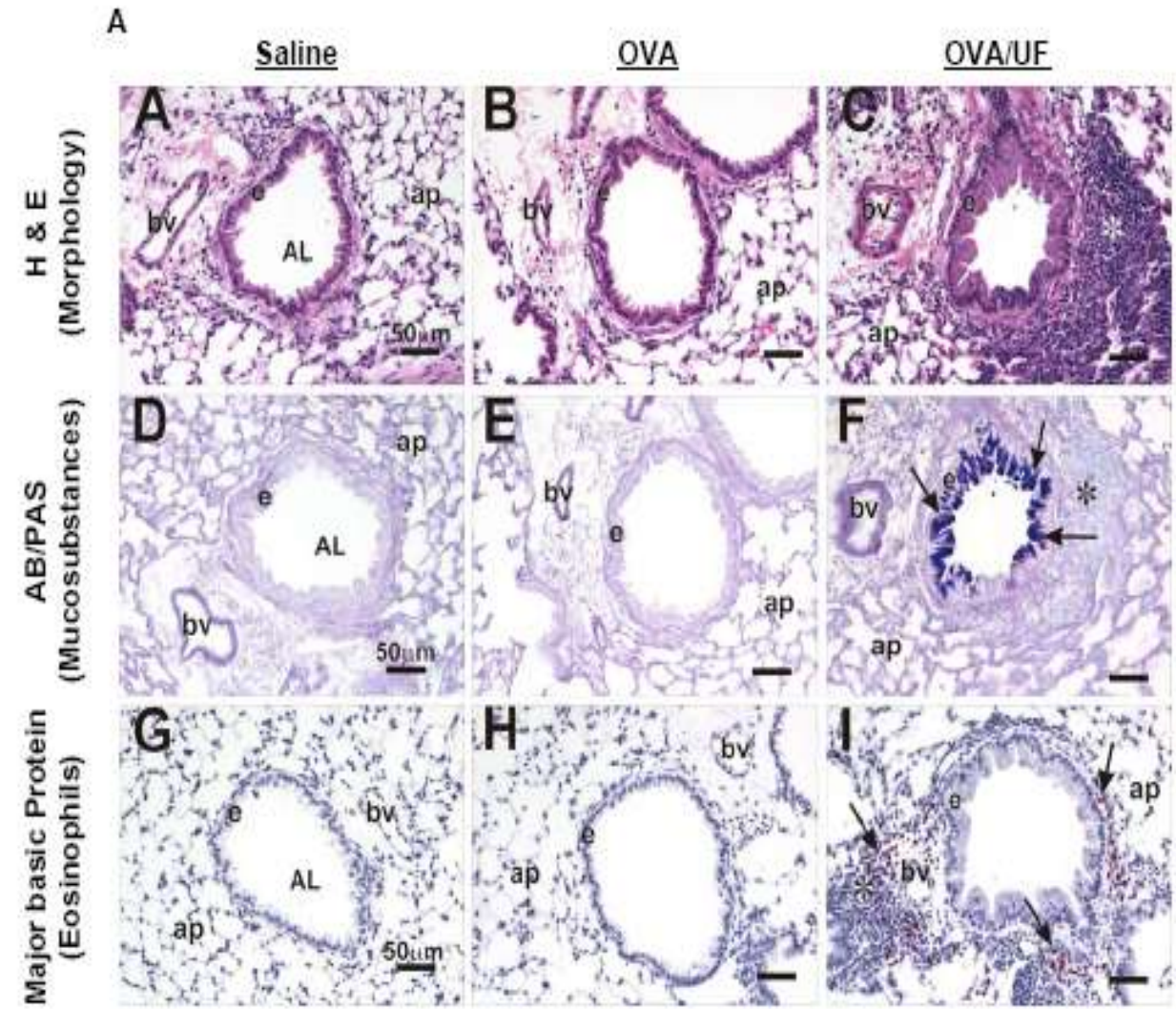


Exposure of Knock-Out Mice to Concentrated Particles (CAPS)

Araujo et al, *Circulation*, 2008

Aortic root sections from UFP mice (C,F) exhibited greater atherosclerotic lesions than sections from Filtered air (A,D) and Fine PM (B,E) mice.

All lesions primarily consisted of macrophages and can be classified as fatty streaks.



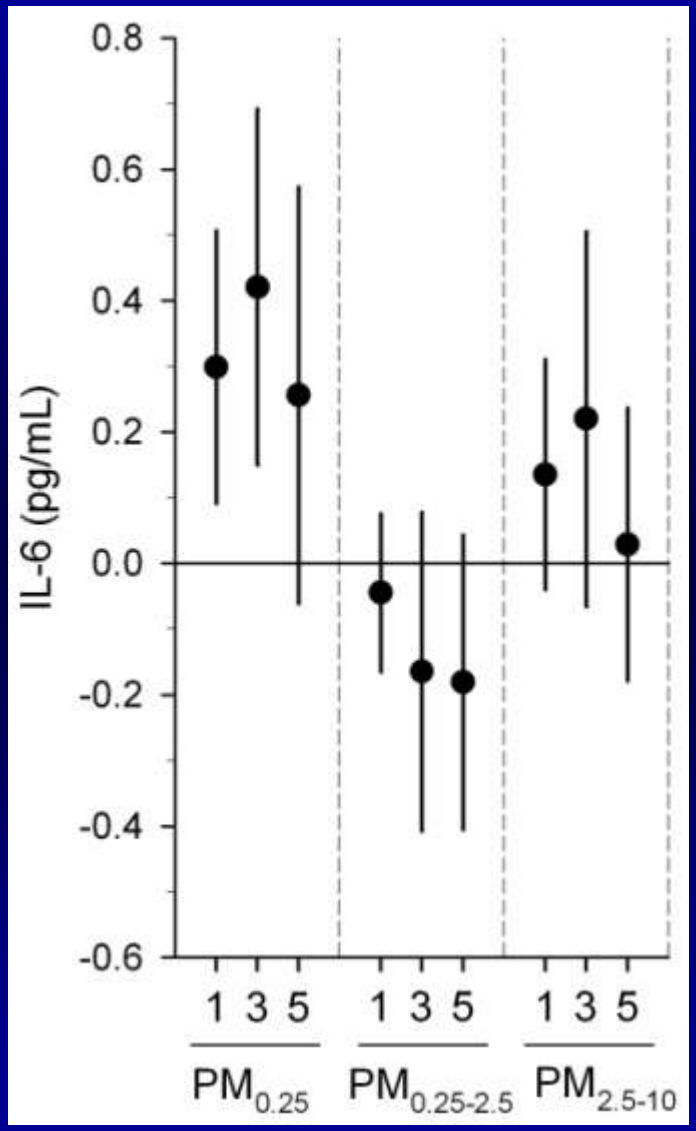
Li et al, EHP, 2009

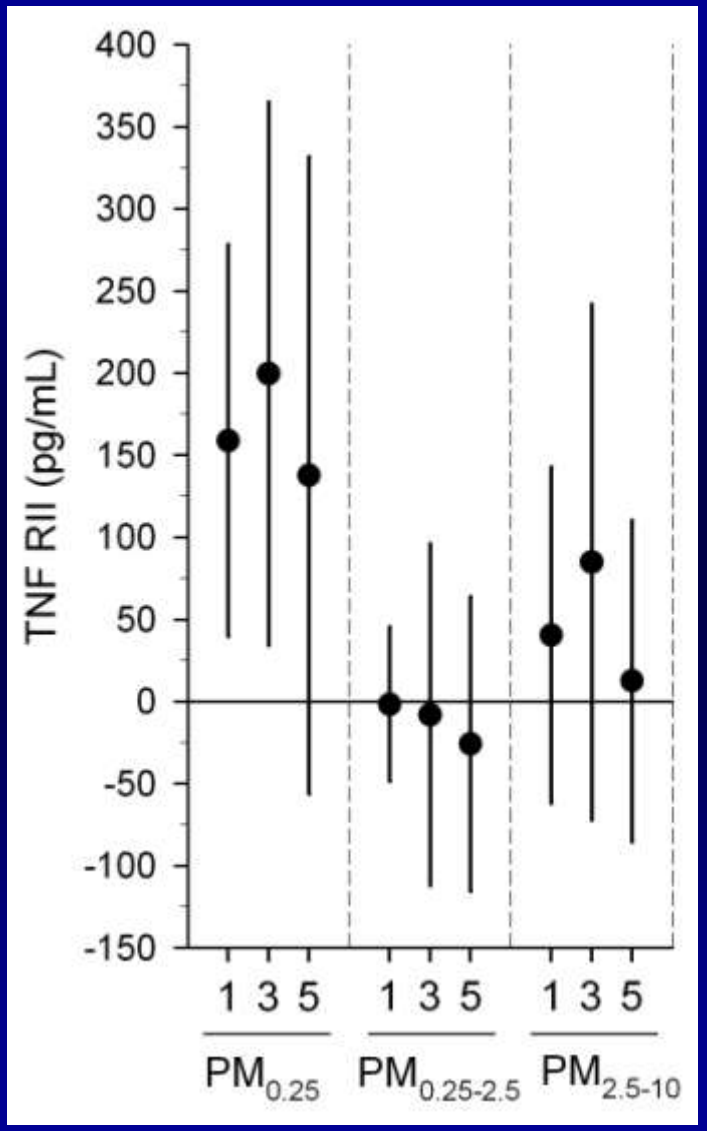
Mice exposed intranasally to:

- Saline (control)
- Ovalbumin (OVA, an experimental allergen)
- OVA +UF particles

Delivery of concentrated ambient ultrafine PM induce ovalbumin (OVA) sensitization and allergic airway inflammation. Allergic inflammation afflicted the nasal turbinates all the way down to the distal pulmonary airways.

Associations of biomarkers of systemic inflammation per Interquartile increase in outdoor size-fractionated particle mass.

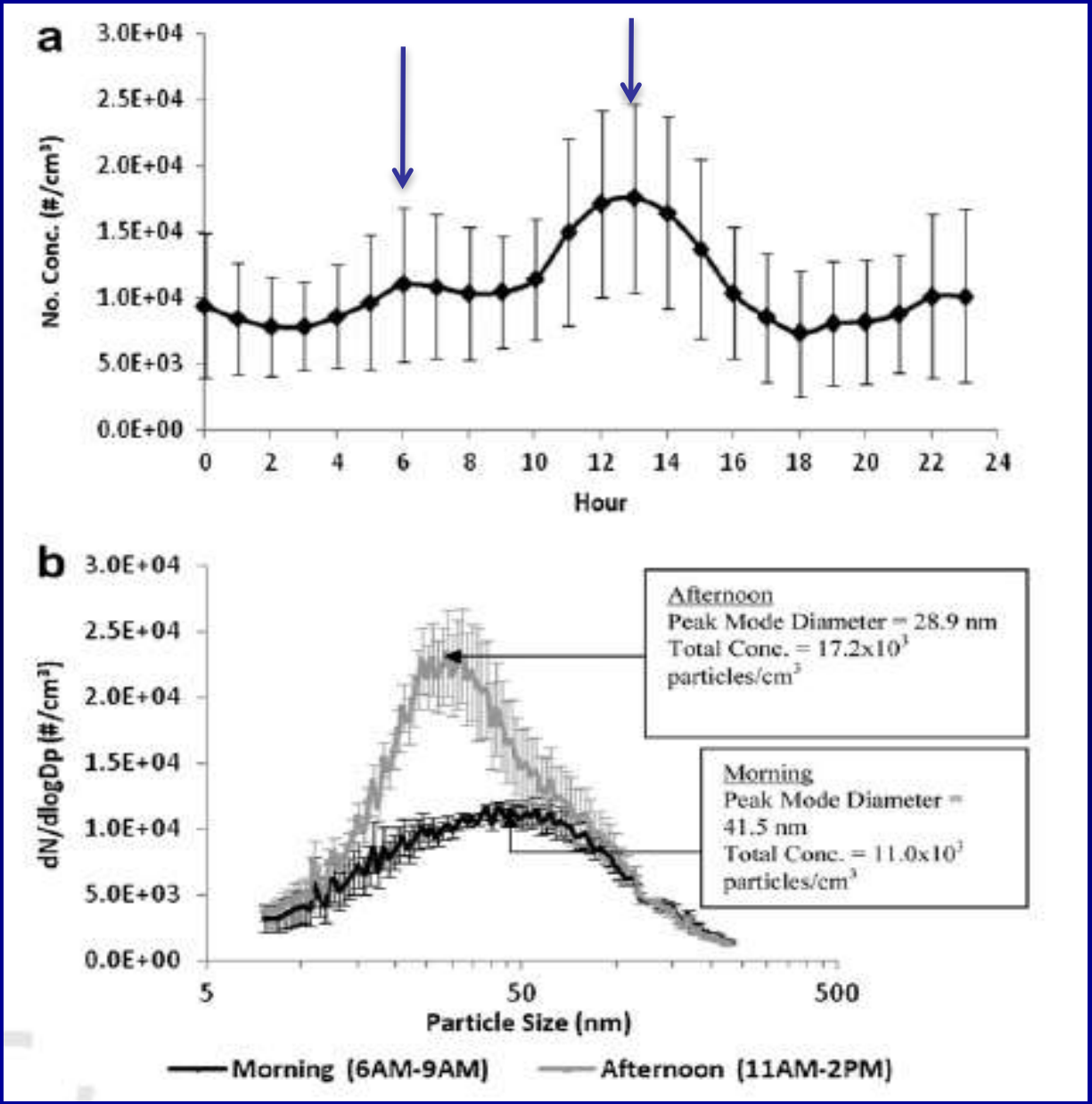




Averages of air pollutants over the previous 5 days

Delfino et al, 2010

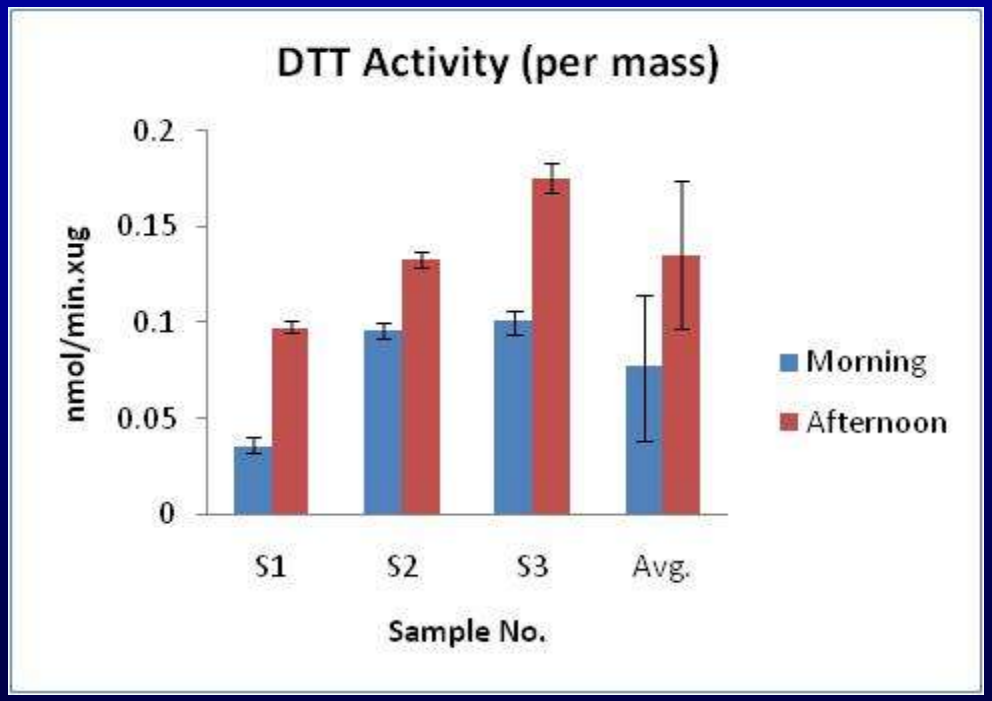
The Role of Atmospheric Aging and Photochemical Processing



Samples in summer period during photochemical periods to distinguish effects from those of PM mostly emitted from mobile traffic sources

Collections from 6-9 am (traffic) and noon- 4 pm (photochemistry)

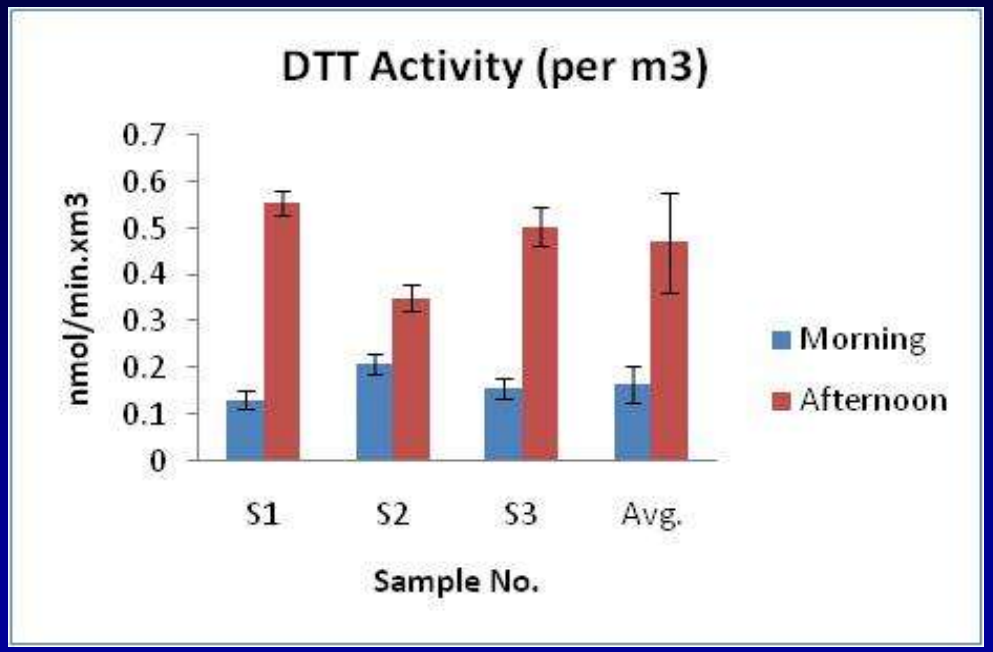
Verma et al, Atmos. Environ, 2009



In vitro studies :

Much higher DTT activity (a measure or redox activity of UFP) in the afternoon than AM (traffic) period expressed both in terms of :

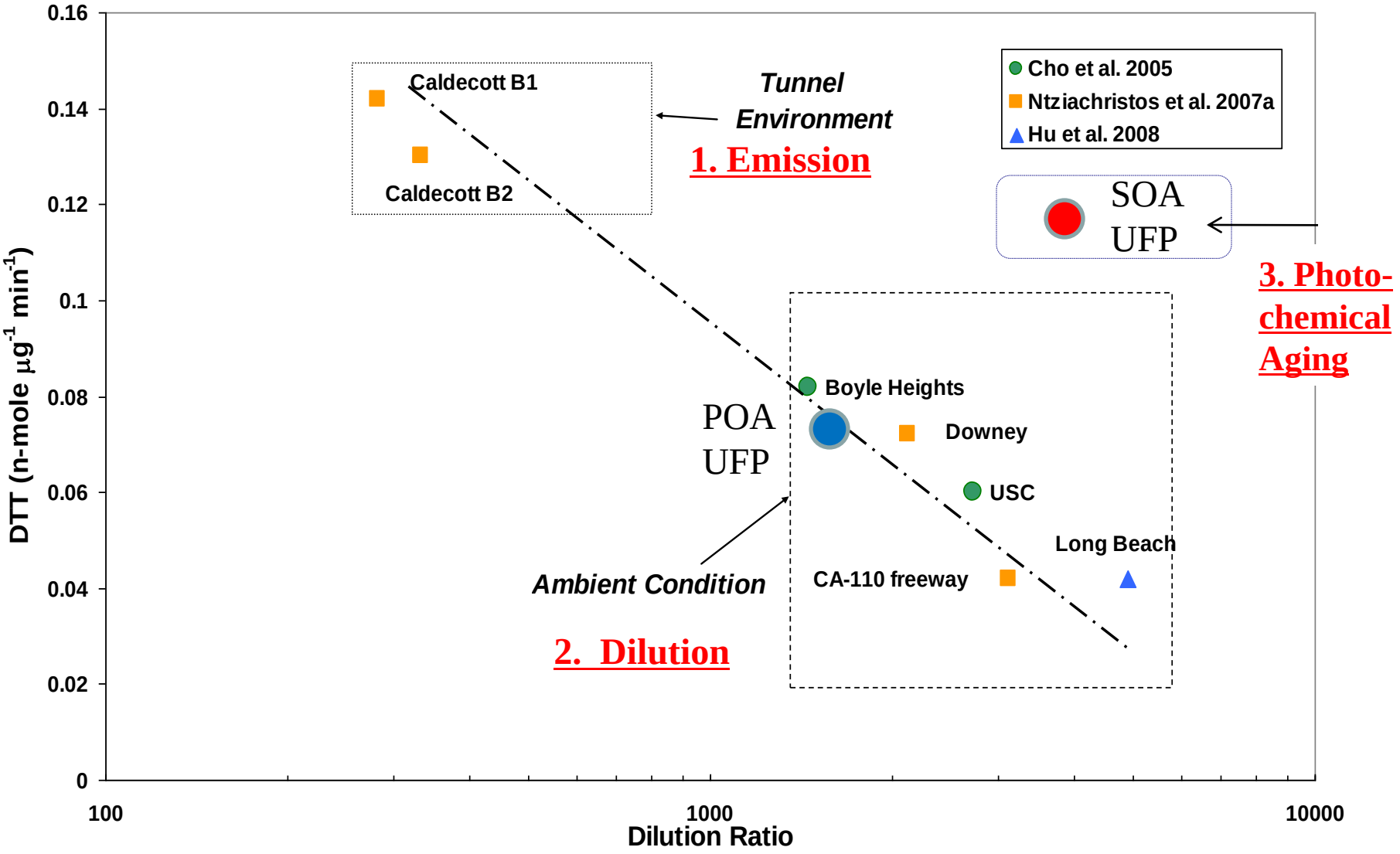
per PM mass



and per m3 of air volume

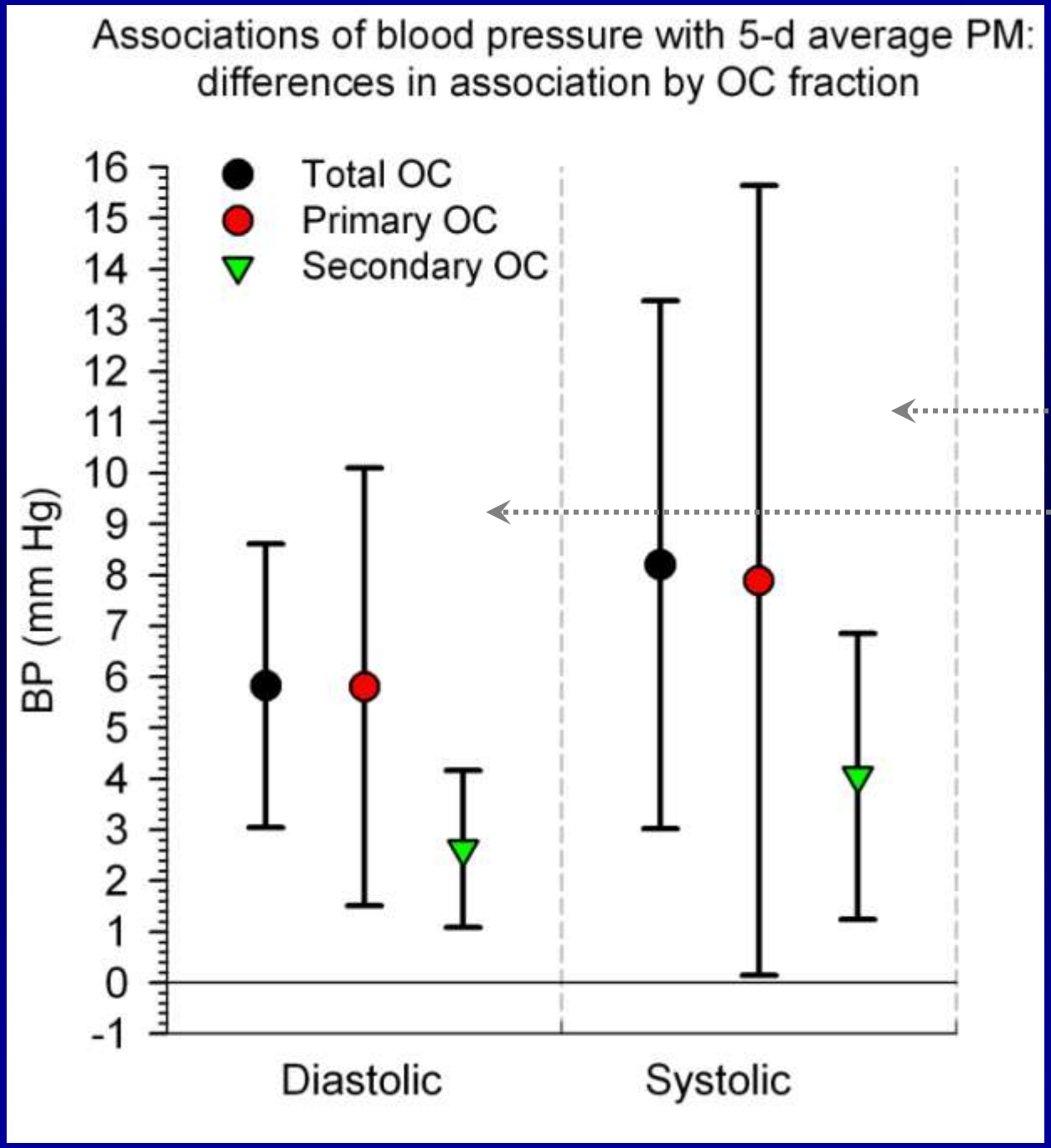
Verma et al,
Atmos. Environ, 2010

Photochemical Aging Modifies Relationship Between Redox Activity and atmospheric dilution (*Verma et al, Atmos Environ 2010*)



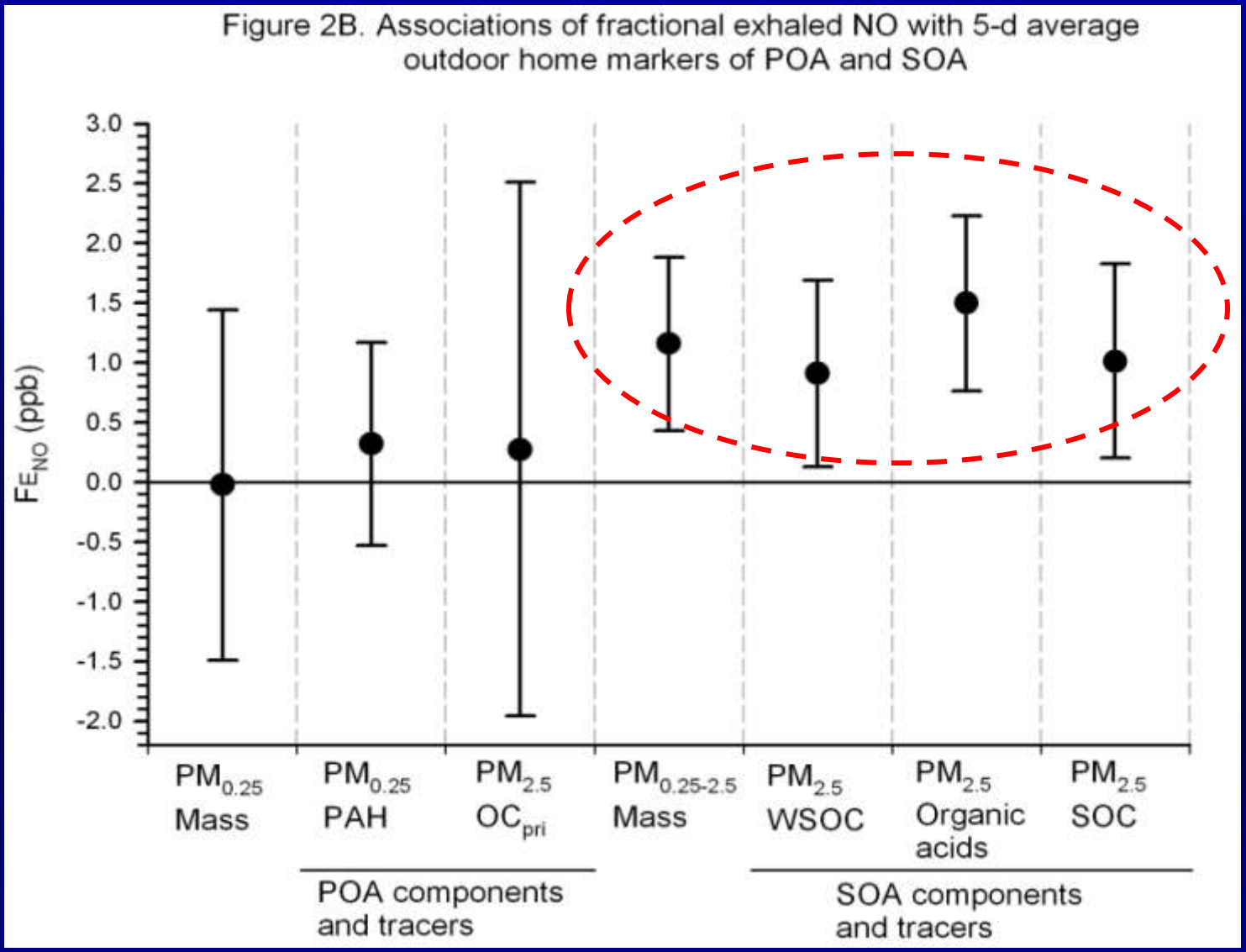
DTT vs Dilution for Primary Organic Aerosols with agreement with other data

DTT vs Dilution for Secondary Organic Aerosols much higher, comparable to tunnel data



The strongest positive associations with blood pressure were for primary (combustion-related) organic carbon

Delfino et al, Epidemiology, 2010



We see significant associations between exhaled NO and markers of secondary organic aerosols (WSOC and Organic Acids) whereas the association with primary aerosols is not significant (*Delfino et al, EHP, 2010*)

Apparatus for Toxicity Studies to Multi- Pollutant Mixture from Traffic Emissions

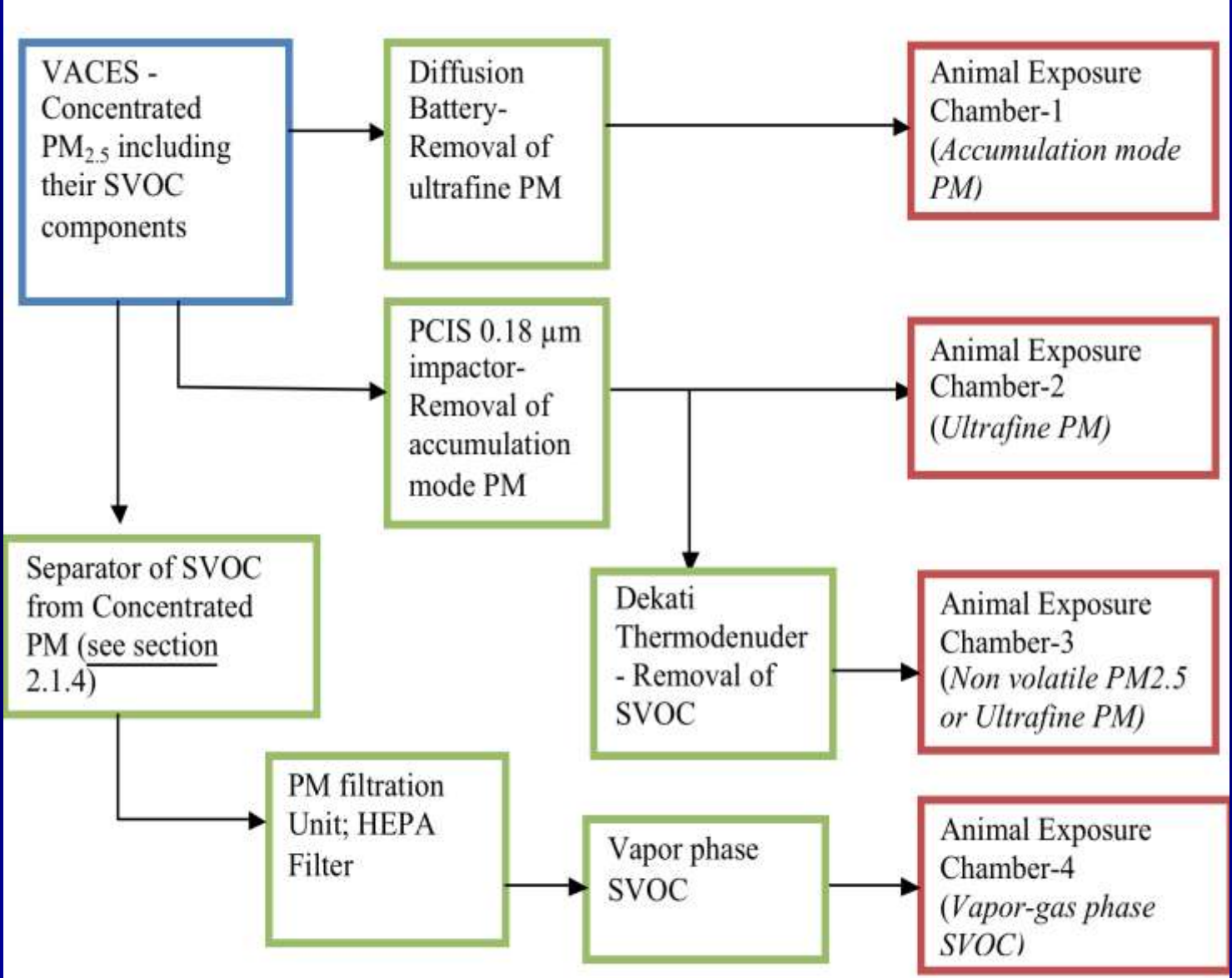
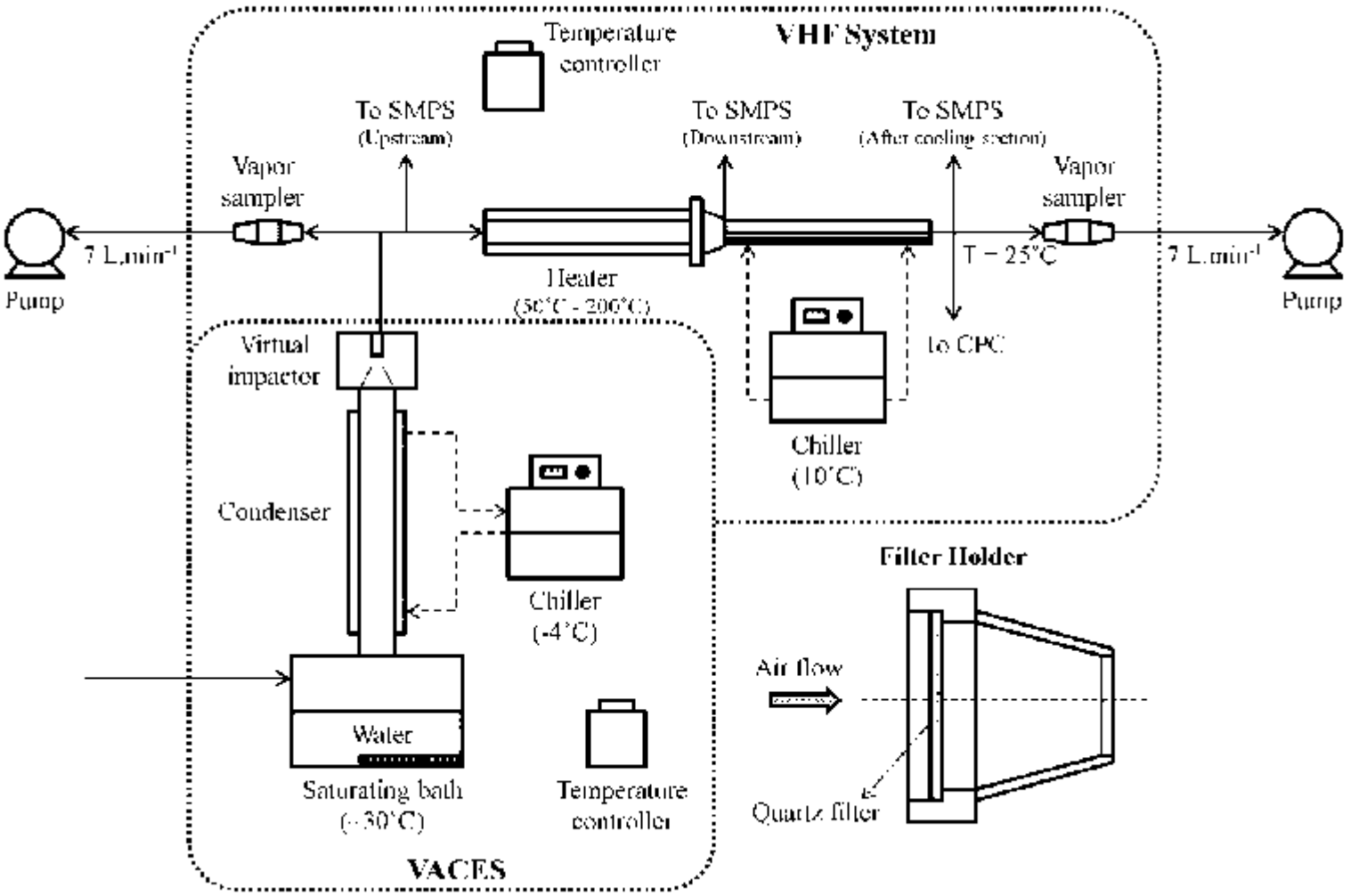


Figure 2- VACES Configurations for Animal Exposures in Project 2



Schematic of Modified VACES for Vapor Phase Only Exposures (*Pakbin et al, J Aerosol Science, 2011*)

Concluding Remarks

- Current vehicle PM emission and ambient pollution standards are based on PM mass measurement.
- Newer vehicles have increased emissions of semi volatile organic compounds (SVOC)nanoparticles, the redox activity of which is much higher than non volatile PM
- These particles may pose a greater risk to public health since they deposit deeper in the human respiratory system and are more redox active
- Further dilution of air parcels from the point of emission drives these SVOC species off the PM phase into the gas phase
- Atmospheric aging and oxidation of these SVOC creates the majority of SOA in urban areas
- A better understanding of the linkages between the SVOC phase, chemistry and toxicity is necessary in order to adopt regulatory strategies that are sufficiently protective to the public.

Research Needs on Evolution of Traffic UFP Emissions

- **Investigation of the atmospheric evolution and aging of multi-pollutants emitted from traffic sources**

- **Focus on the following categories of pollutants:**
  - **size fractionated and chemically speciated PM_{10} (including semi-volatile components)**
  - **thermally denuded of their semi-volatile components speciated non-volatile PM**
  - **vapor phase semi-volatile organics (SVOC)**

Types of Studies to be Conducted

- ***in-vitro* (cellular and molecular)**
- ***in-vivo* (instillation and inhalation exposure) studies focusing on respiratory, cardiovascular and neurological outcomes**
- **Eventually panel studies since we also have ways of measuring separately each of the above groups of pollutants**

Acknowledgements

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