26th ANNUAL AEROSOL CONFERENCE

American Association for Aerosol Research, Sept 24 – 18, 200 Reno, NV

Session 4D: Combustion

Nucleation Mode Particle Emissions from In-use Heavy Duty Vehicles Equipped with DPF and SCR Retrofits

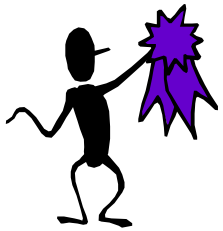
Jorn Dinh Herner[1], Alberto Ayala[1], William Robertson[1], Oliver Chang[1], Subhasis Biswas[2], and Constantinos Sioutas[2]

[1]*California Air Resources Board*

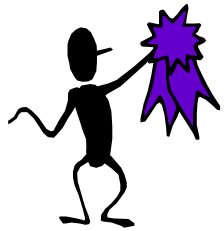
[2]*University of Southern California*

California Environmental Protection Agency

Air Resources Board



Acknowledgements:



CARB Staff: Keshav Sahay, John Karim, Ralph Rodas, George Gatt, Paul Rieger, Christine Maddox, and many more..

USC: Shaohua Hu, Vishal Verma

Co-Sponsors:

California Energy Commission

SOUTH COAST AQMD

In Kind Contributors:

CALIFORNIA DEPARTMENT OF TRANSPORTATION

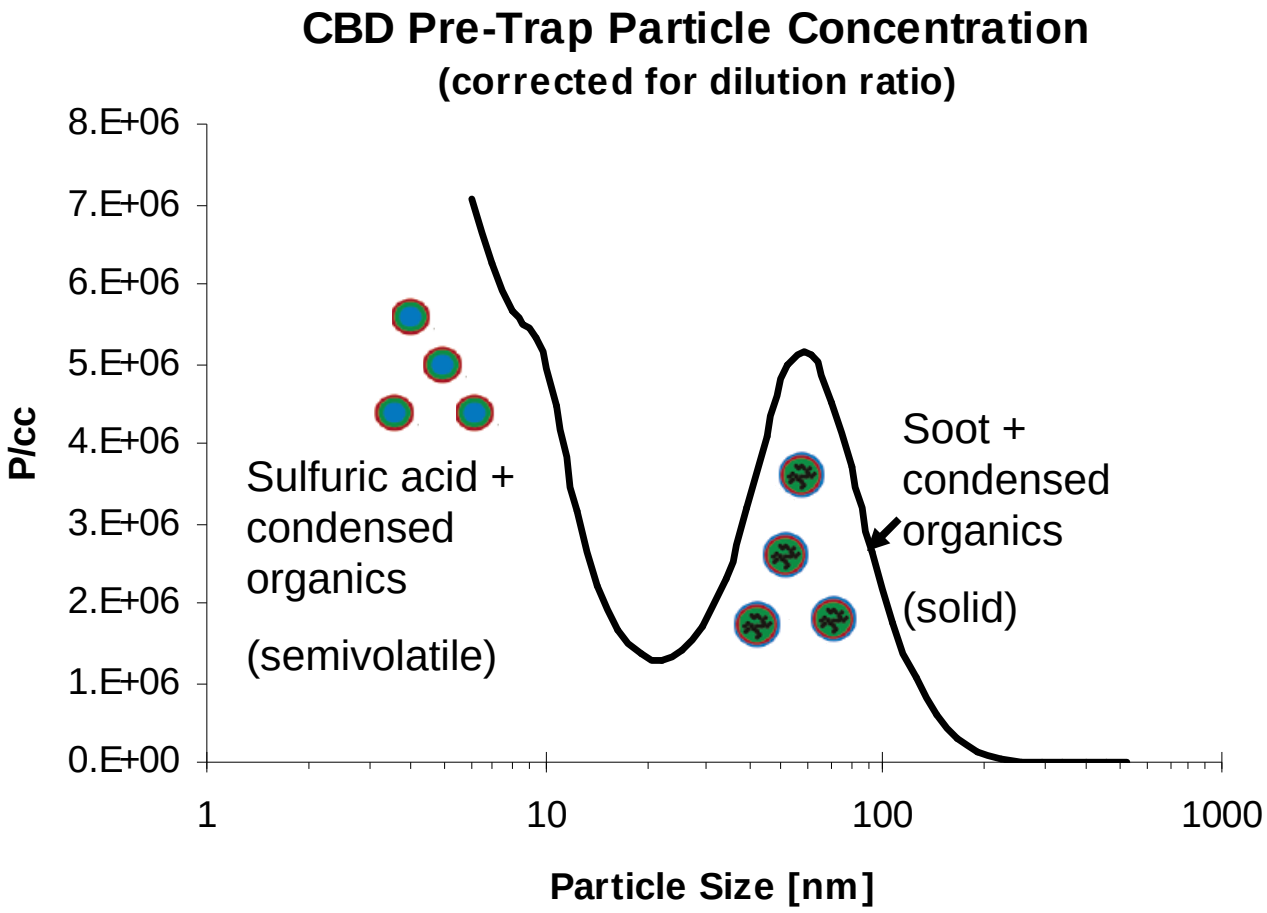
D.A.R.T. Downey Area Recycling & Transfer

ELK GROVE Unified School District

SAN JOAQUIN RTD

bp

Diesel Particulate Matter Emissions



- Within the ultrafine range two modes exist in diesel emissions
  1. Solid soot particles in the accumulation mode.
  2. Semivolatile nucleation mode (nanoparticles)

Experimental Setup
CARB Heavy-duty Diesel Emissions Test Laboratory

- **Ultra Low Sulfur Diesel (7ppm)**
- **CVS - Dilution Tunnel**

- **Real time particle measurements:**
  EEPS, DMS500, SMPS, CPC's, DC, PAS
- **Cycles:**
  Cruise at 50mph, UDDSx2, Idle (**only cruise discussed here**)

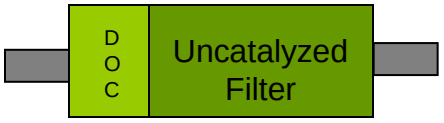
Test Matrix - 1/2
4 vehicles, 8 configurations

Veh#1

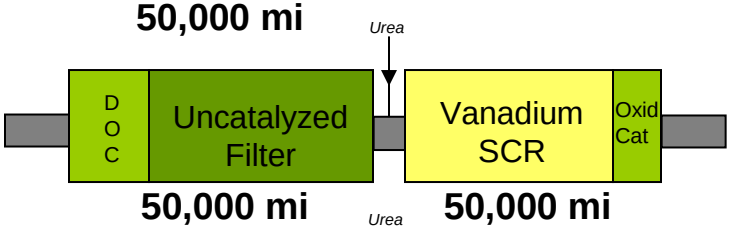
1998 Cummins Diesel
11L, 360,000 miles

No Aftertreatment - Baseline

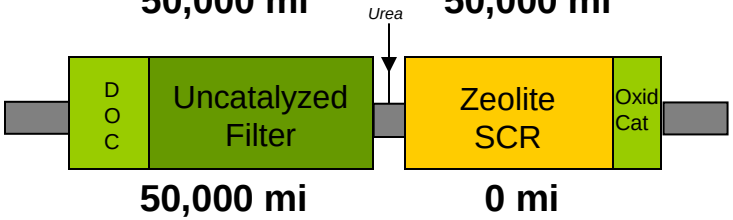
Veh#1
Baseline



Veh#1
CRT1®



Veh#1
V-SCRT®*

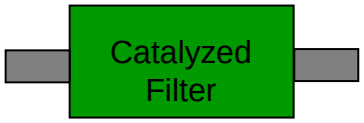


Veh#1
Z-SCRT®*

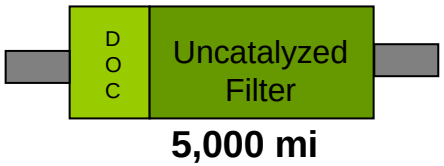
*** SCRT® systems used in this project are development prototypes not commercial units.**

Veh#2

1999 International Diesel
7.6L, 40,000 miles



Veh#2
DPX

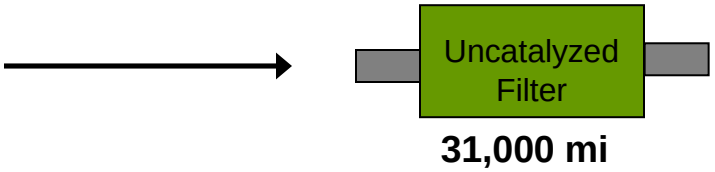


Veh#2
CRT2®

Test Matrix - 2/2
4 vehicles, 8 configurations

Veh#3

2003 Cummins Diesel
5.9L, 50,000 miles

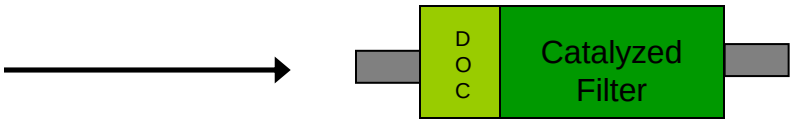


31,000 mi

Veh#3
Horizon

Veh#4

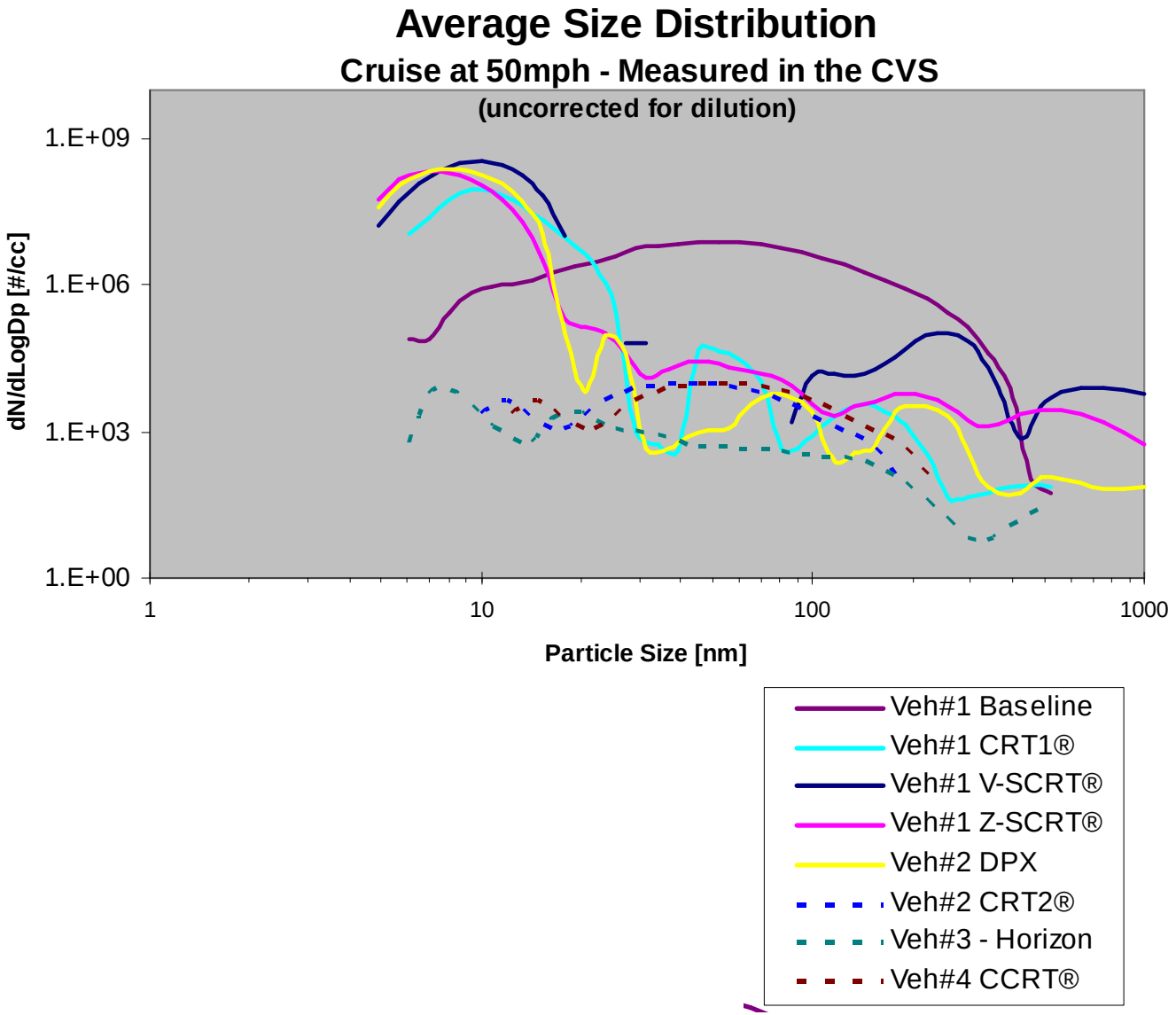
2006 Cummins Diesel
w/ Allison Hybrid drive
5.9L, 1,000 miles



1,000 mi

Veh#4
CCRT®

Average Size Distribution



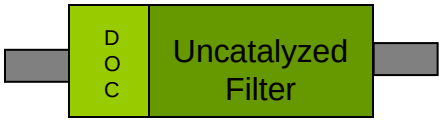
<u>Accumulation mode seen in:</u>
Veh#1 Baseline

<u>nucleation mode seen in:</u>
Veh#1 CRT1®
Veh#1 V-SCRT®
Veh#1 Z-SCRT®
Veh#2 DPX

<u>No nucleation mode in</u>
Veh#1 Baseline
Veh#2 CRT2®
Veh#3 Horizon
Veh#4 CCRT®

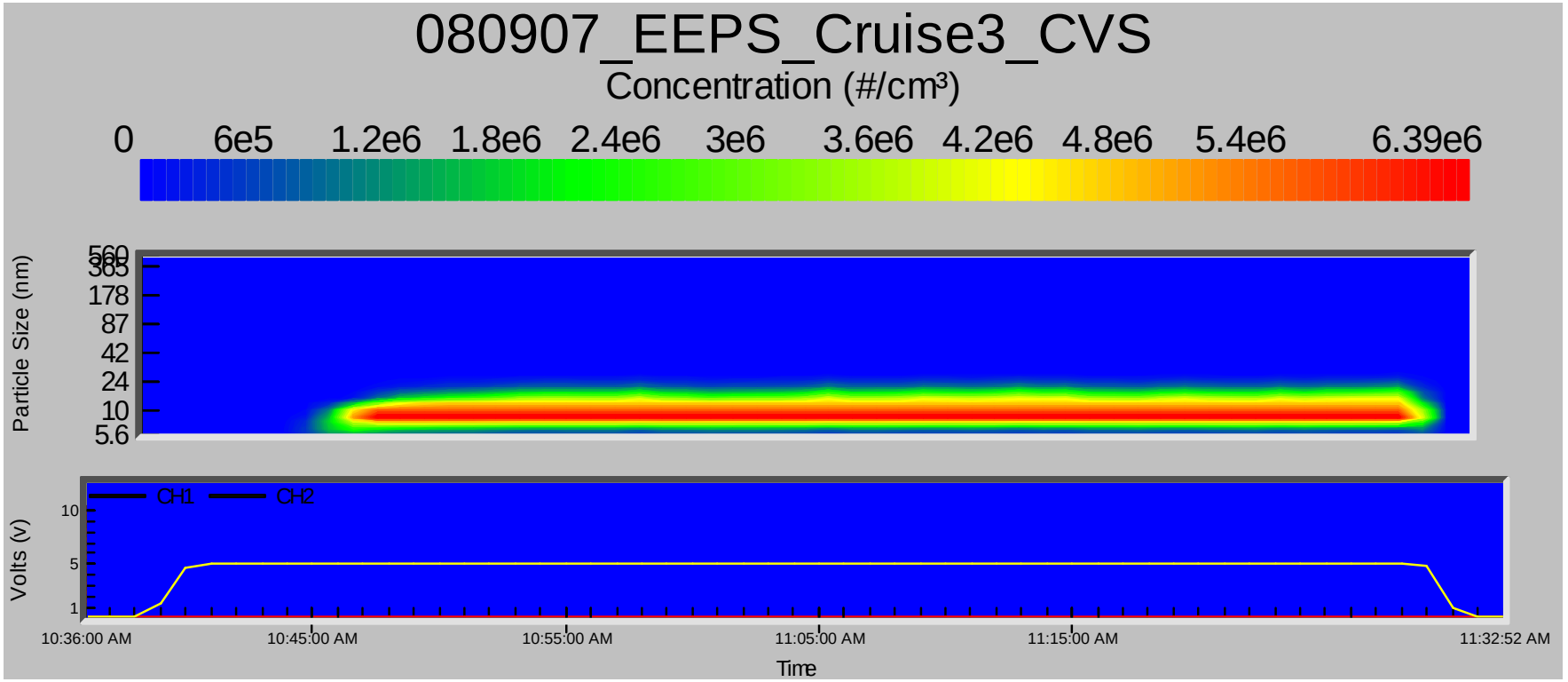
Real Time Size Distribution

in the dilution tunnel



50,000 mi

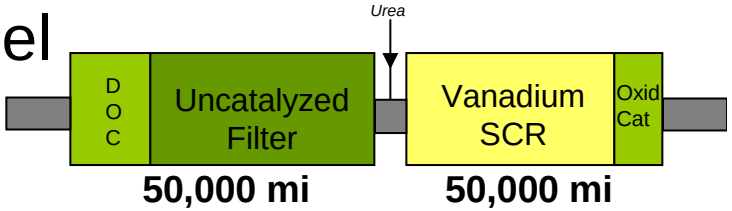
Veh#1 CRT1®



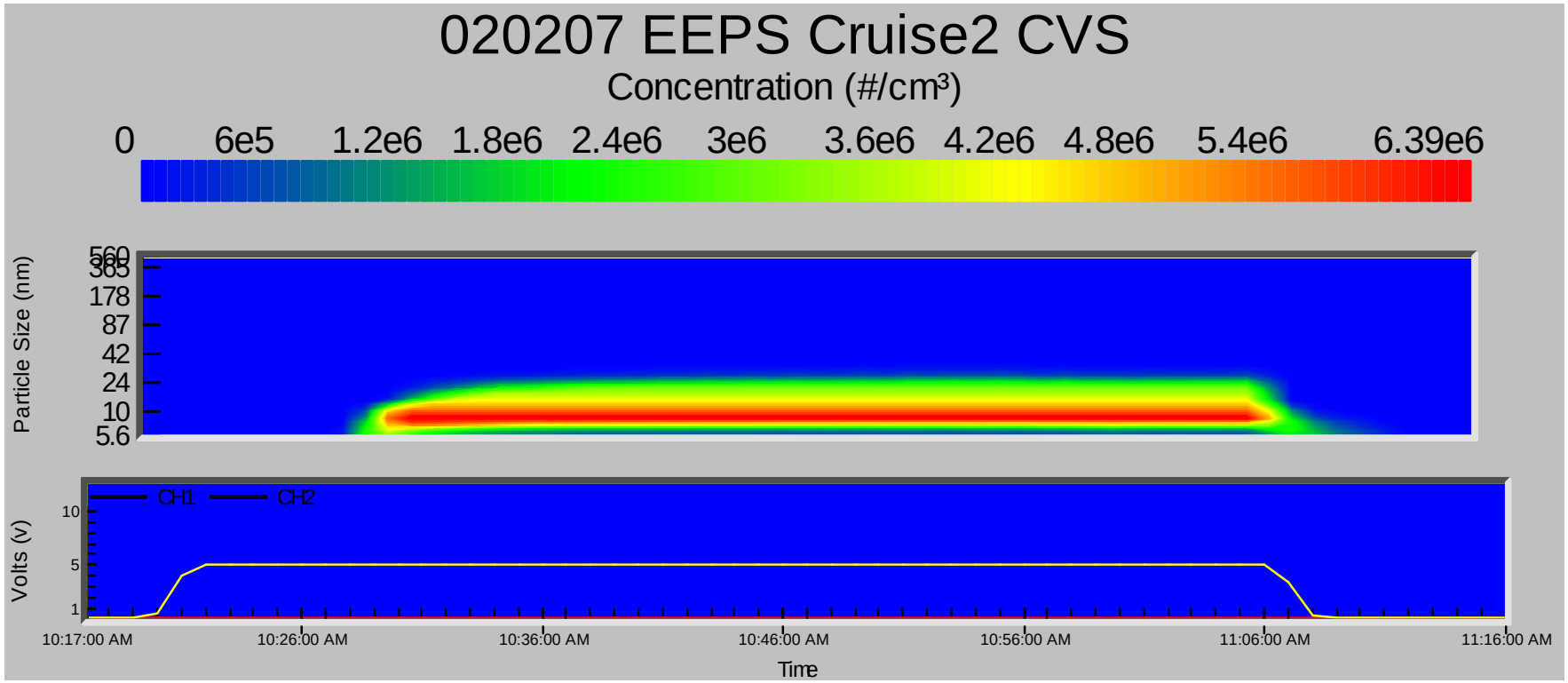
Nucleation mode starts 5-10 min after the cruise is started and remains unchanged until the cycle ends.

Real Time Size Distribution

in the dilution tunnel



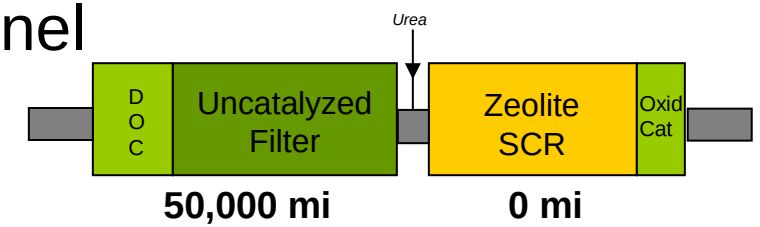
Veh#1 V-SCRT®



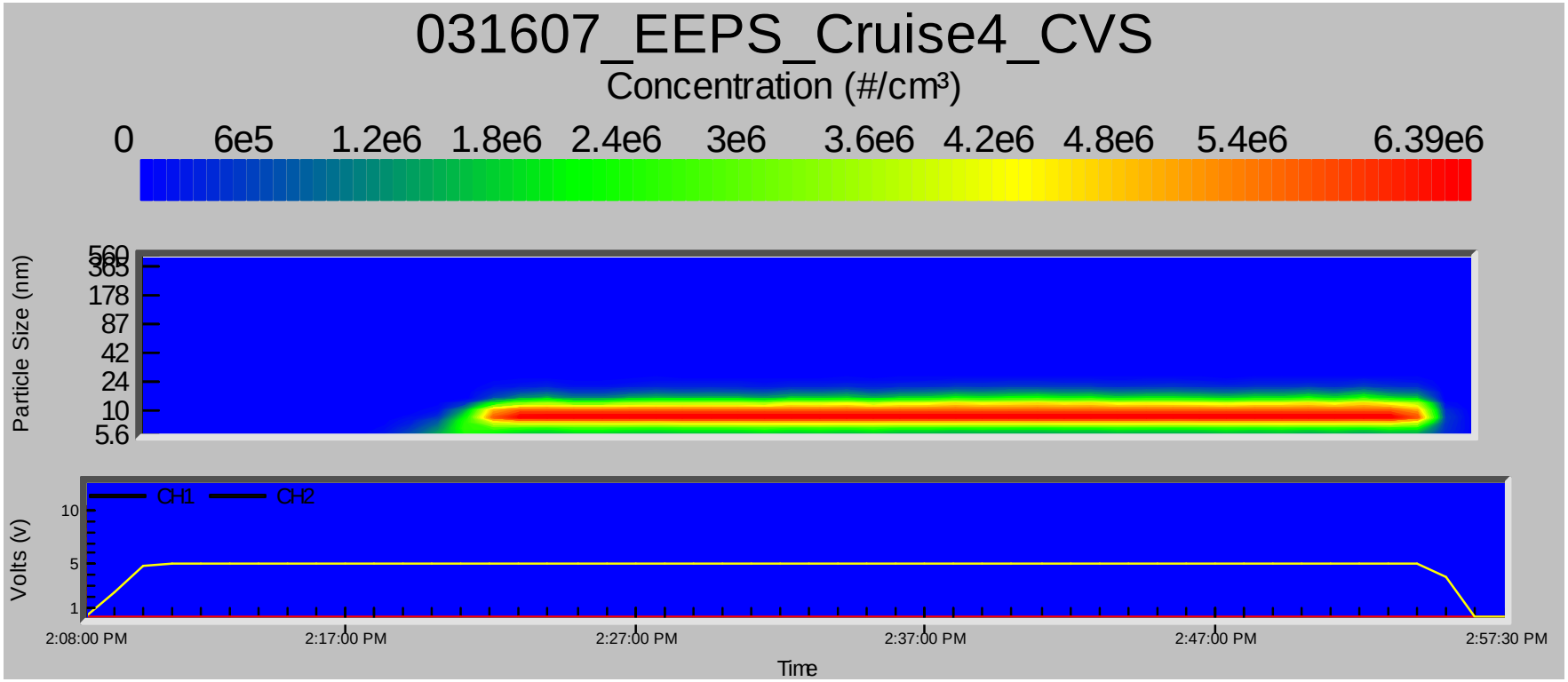
Nucleation mode starts 5-10 min after the cruise is started and remains unchanged until the cycle ends.

Real Time Size Distribution

in the dilution tunnel



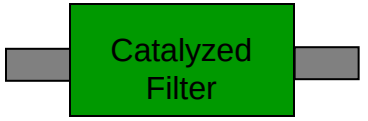
Veh#1 Z-SCRT®



Nucleation mode starts 5-10 min after the cruise is started and remains unchanged until the cycle ends.

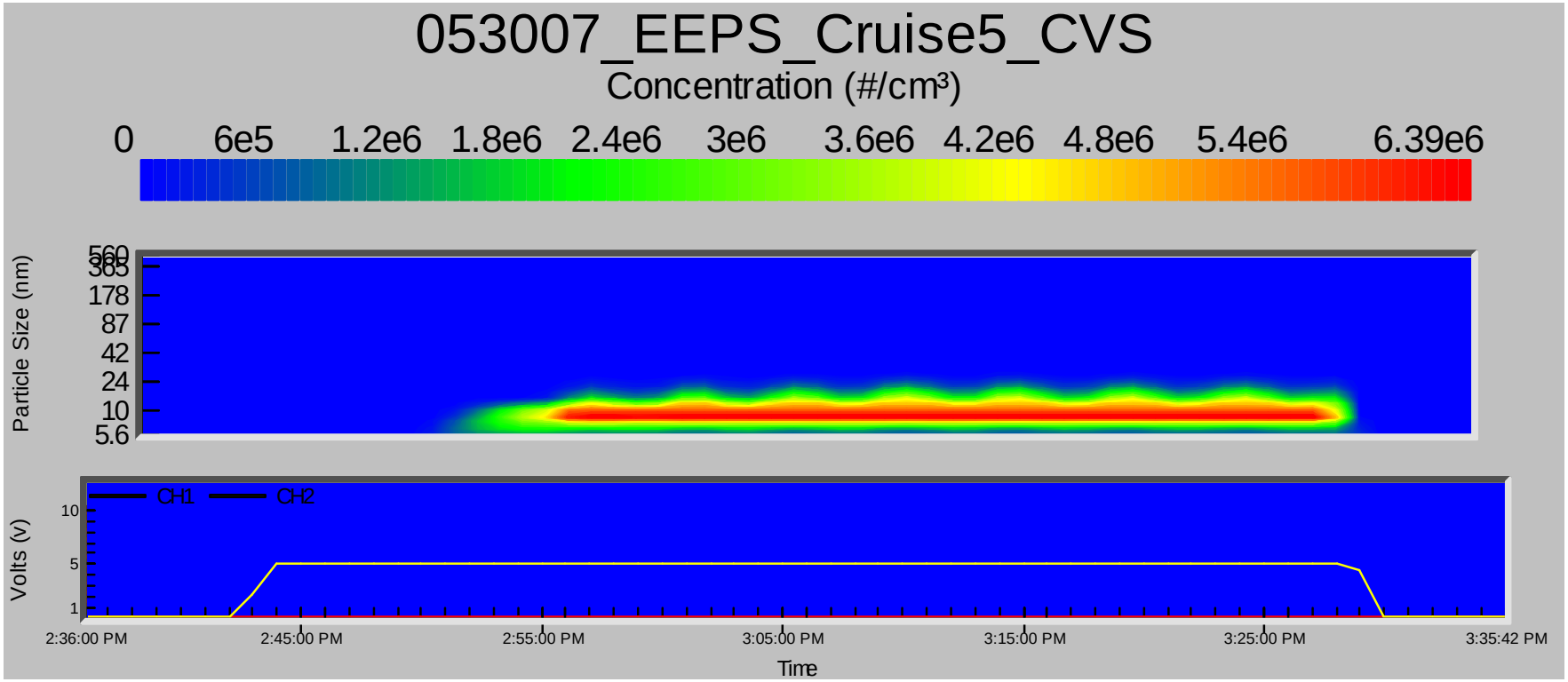
Real Time Size Distribution

in the dilution tunnel



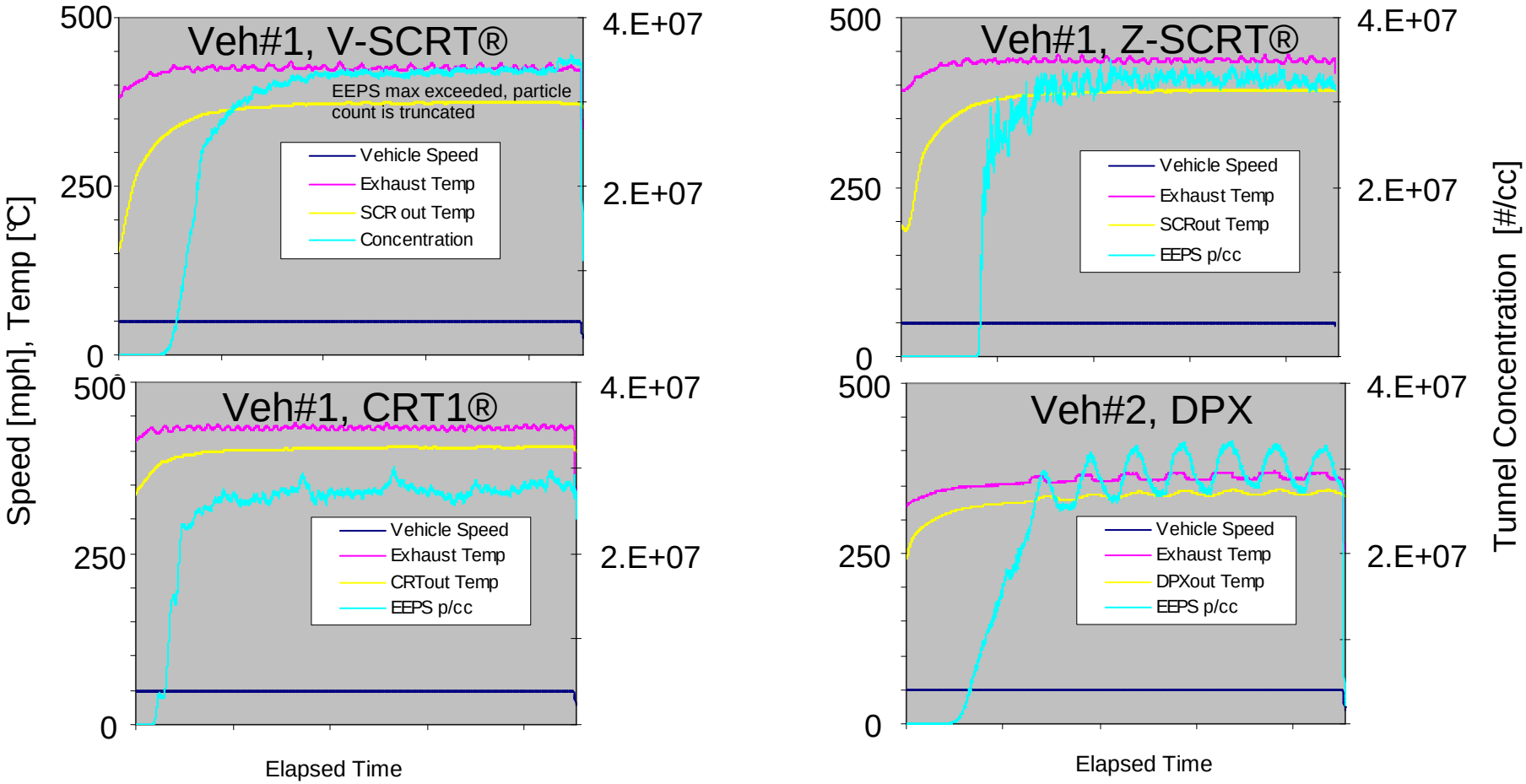
30,000 mi

Veh#2 DPX



Nucleation mode starts 5-10 min after the cruise is started and remains unchanged until the cycle ends.

Nucleation is Temperature Dependent



Each configuration emits nucleation mode particles once the post-aftertreatment exhaust reaches a critical temperature:

T_{crit} Veh#1, V-SCRT® = 330ºC

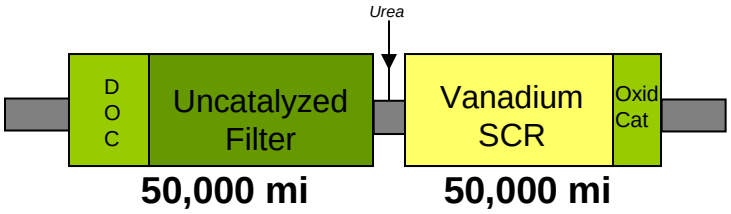
T_{crit} Veh#1, CRT1® = 373ºC

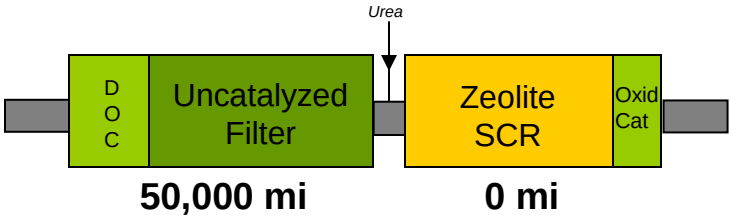
T_{crit} Veh#1, Z-SCRT® = 373ºC

T_{crit} Veh#2, DPX = 315ºC

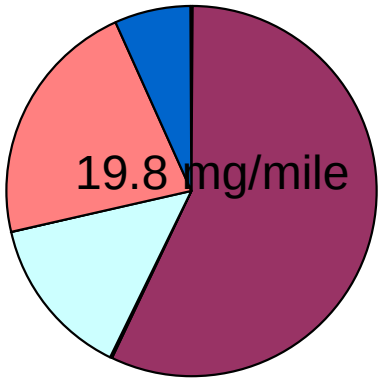
Chemical Composition of PM

Cruise cycle

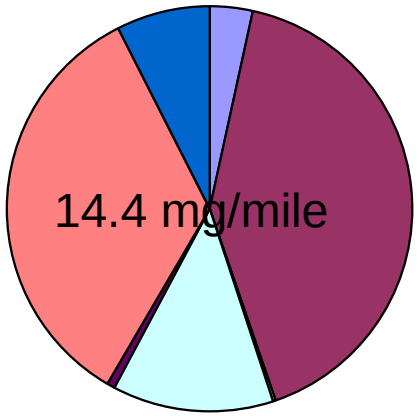


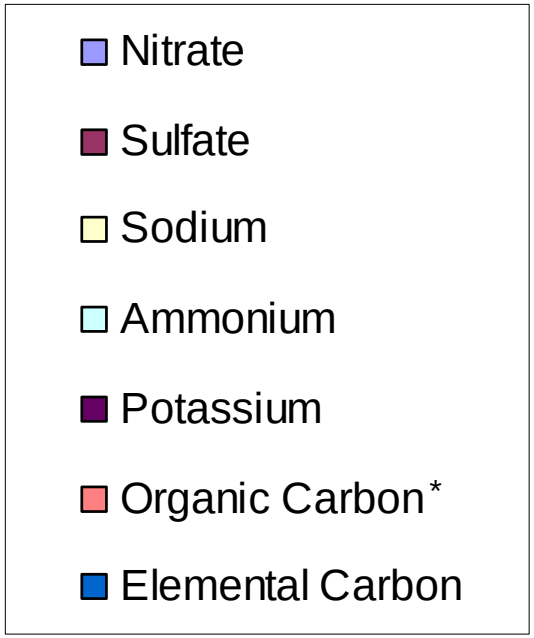


Veh#1, V-SCRT®



Veh#1, Z-SCRT®





* No correction for gas-phase adsorption or oxygen/hydrogen species

40-60% of PM is Sulfate

Sulfur in Combustion

Fuel/Oil Sulfur$_{(li)}$

Instant **Temp and RH**
(dilution ratio)

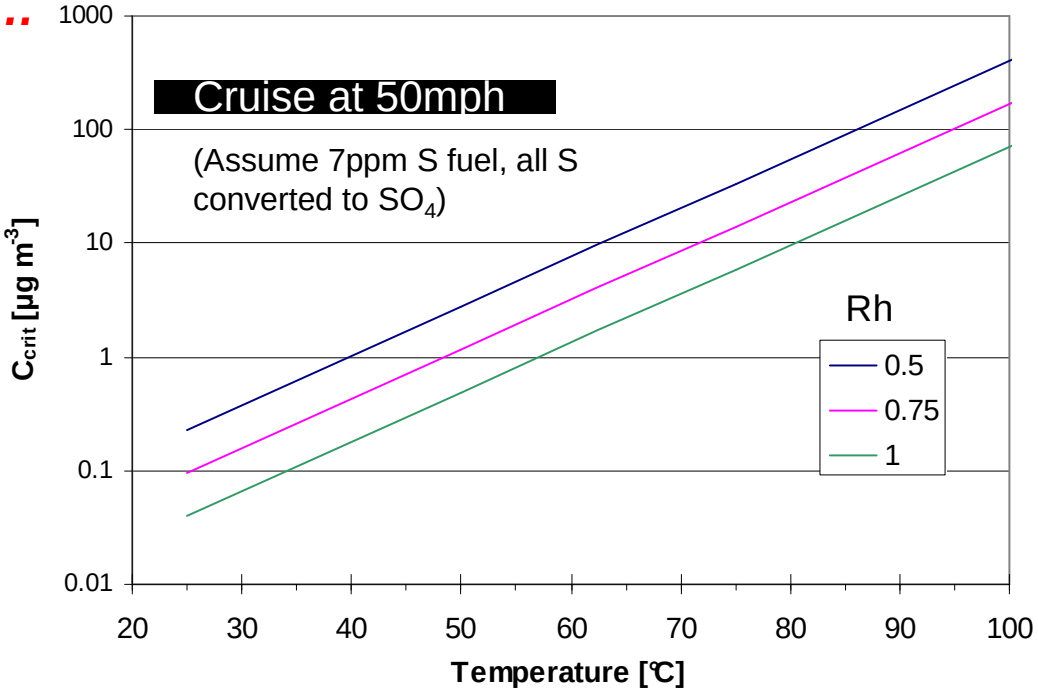
$$SO_{2(g)} \xrightarrow{H_2O} SO_{3(g)} \rightarrow H_2SO_{4(g)} \rightarrow \bullet \; H_2SO_{4(p)}$$

In the presence of ammonia will also form
$NH_4HSO_{4(p)}$, $(NH_4)_3H(SO_4)_{2(p)}$, $(NH_4)_2(SO_4)_{(p)}$

Limiting Step in nucleation…

C_{crit} = 0.16exp(0.1T-3.5Rh-27.7)

Where,
C_{crit} = gas concentration at which sulfate nucleates [µg m^{-3}]
T = ℃elvin
Rh = Relative humidity [0-1]

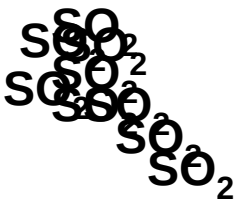


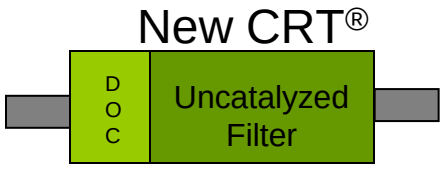
A Conceptual Model for Nucleation

effect of catalytic surfaces

- Storage
  - "Fresh catalytic surfaces can store sulfate"

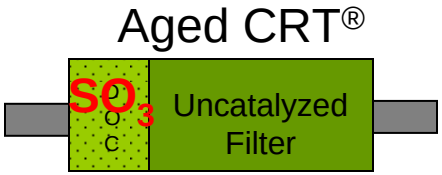
    Kittelson et al, Journal of Aerosol Science, Sep2006, Vol. 37 Issue 9, p1140-1151



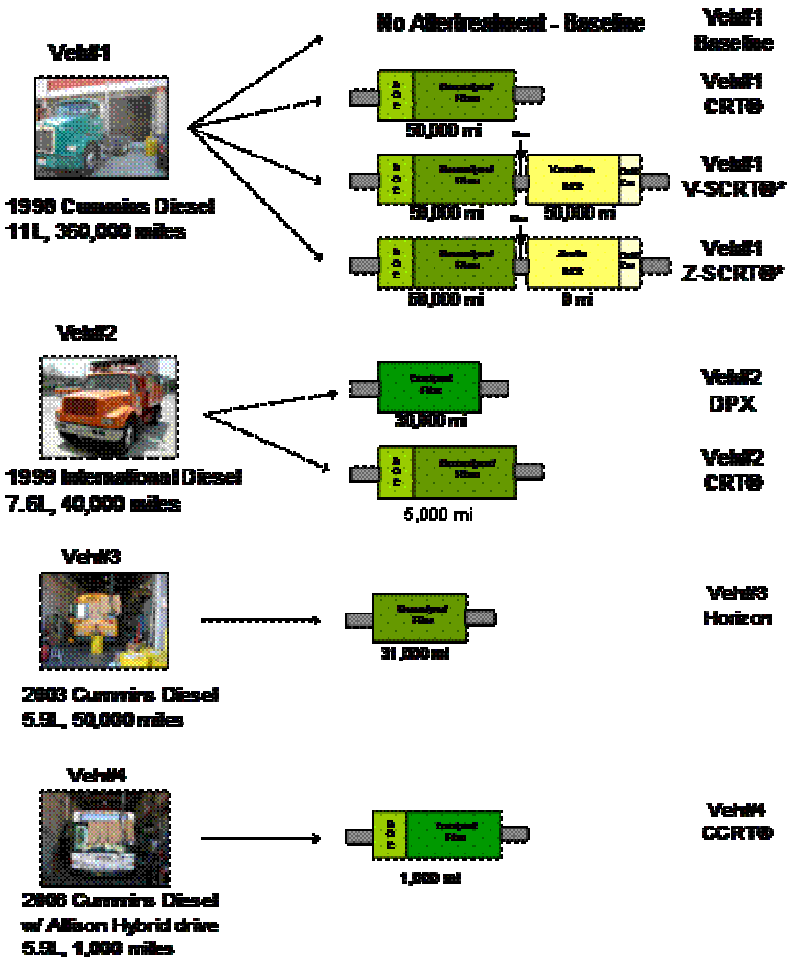


- SO_2 to SO_3 conversion
  - Catalytic surfaces affect SO_2 to SO_3 conversion
  - Conversion is temperature dependent

    Cooper & Thoss SAE 1989 No. 890404, 171-183



Summary



Vehicles equipped with aftertreatment devices that have been degreened and contain catalytic surfaces emit a nuclation mode.

Conclusions

- Catalyzed surfaces can initially store SO_2
- Catalyzed surfaces reduces the temperature at which SO_2 is converted to SO_3 to levels seen in vehicle exhaust during cruise and transient cycles
- The temperature at which SO_2 is converted to SO_3 is device specific and very discreet
- The conversion of SO_2 to SO_3 was rate limiting in nucleation mode formation in the current study (as opposed to dilution ratios)
- More research needed to determine the storage capacity of catalyzed surfaces
- Should the conceptual model developed using ambient and uncontrolled diesel PM suggesting that particle number is a surrogate for toxicity be applied to nucleation mode sulfur based particles ?

Thank you
Questions ?

See also at AAAR

From the same project:

2F.2 Tuesday 9:15 pm: *Towards 2010 NOx and PM emission Levels: Overview of CARB's Investigation of Advanced Heavy–duty On-road Vehicle Retrofits and Other Technologies.*

5D.4 Tuesday 4:35 pm: *Physical Properties of Particulate Matter (PM) from Newer Heavy Duty Diesel Vehicles Operating with Advanced Emission Control Technologies.*

11M.7 Thursday 9:15 am: *Chemistry of Air Toxics Emitted from In-use Heavy Duty Vehicles Equipped with DPF and SCR Retrofits*.