Trends in Size-Fractionated Particle Number and Mass Emission Factors from Light and Heavy Duty Vehicles in California and Health Implications

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Background and Introduction :

- There has been rapidly increasing epidemiological and toxicological evidence linking cardio-respiratory health effects and exposures to ultrafine particles (Peters et al., 1997; Pekannen et al. 1997; Li et al., 2002 and 2003; Xia et al., 2004)

- Emission inventories suggest that motor vehicles may be the primary direct emission sources of fine and ultrafine particles to the atmosphere in urban areas (Hitchins et al., 2000; Zhu et al, 2002a).

- PM from Mobile Sources ; major thrust are of the SCPCS.

- Emphasis on : particle emission levels, particle transport and transformation away from the source --- busy roads and freeways, penetration to indoor environments, ultimately health effects

- This presentation summarizes research findings of the SCPCS, funded by the US EPA and the California ARB, seeking to provide information on emission factors for different PM size ranges and for different vehicle types, while determining any changes in HDV and LDV emission factors since 1997

Our Tunnel Measurements (Geller et al, ES&T, 2005 accepted for publication)

- Location: Caldecott tunnel in between Orinda and Berkeley, CA.
- The tunnel has two bores—one restricted to gasoline vehicles (LDV) and one 3.8% heavy-duty diesel vehicles (HDV).
- Emissions were apportioned to either HDV or LDV sources and emission factors calculated.
- Data compared to the Kirchstetter et al. study of 1997

Experimental Matrix

- Bore 1 (mixed vehicles) and Bore 2 (gasoline only)
- Entrance (background) and Exit (contribution of tunnel traffic)
- One week (September 2004) in each bore
- Sampling interval: 12 PM – 6 PM

Pollutants Sampled

- Carbon monoxide (CO), Carbon dioxide (CO2)
- Traffic (vehicle) counts by bore
- Particle size distributions (7 nm – 500 nm)
  - SMPS Model 3081 (TSI)
  - CPC Model 3022 (TSI)
- Coarse (2.5-10μm), accumulation (0.15 - 2.5μm) and ultrafine (<0.15μm) PM mass
  - MOUDI
  - Tri-mode high volume impactor train (*Misra et al. JAS 2002*)
- Chemical speciation: elemental/organic carbon, EC/OC, nitrate, sulfate, metals and elements, PAH, organic molecular tracers

Daily Pollutant Concentrations

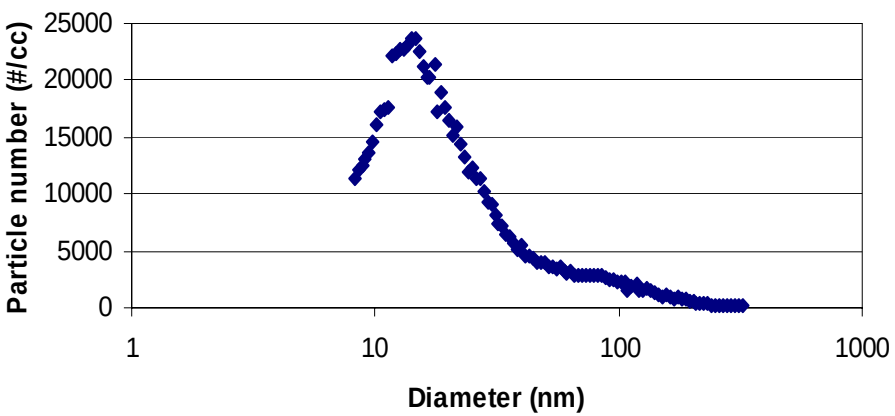
Table 4. Pollutant concentrations measured in the Caldecott tunnel. PM_{10} mass over-balances are due to the substantial organic adosption artifact on the ultrafine quartz filter (*).

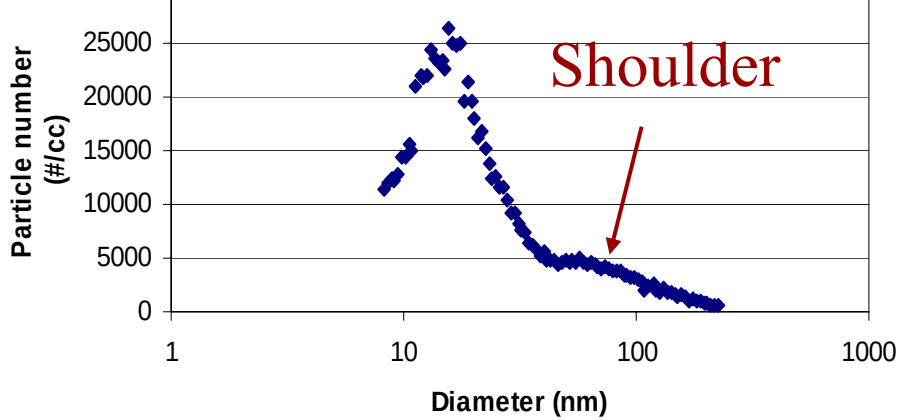
Bore and Sampling Time	Date	Average CO (ppm)	Average CO_2 (ppm)	PM_{10} mass ($\mu g/m^3$)	PM_{10} EC ($\mu g/m^3$)	PM_{10} OC* ($\mu g/m^3$)	PM_{10} SO_4^{2-} ($\mu g/m^3$)	PM_{10} NO_3^- ($\mu g/m^3$)	Average Particle Numbers ($\#/cm^3$)
Bore 2 (12-18 h) (gasoline only)	23-Aug-04	10.5	413	14.9	8.2	14.0	0.36	0.71	5.5×10^5
	24-Aug-04	9.2	352	18.9	6.0	22.9	1.22	0.11	6.9×10^5
	25-Aug-04	10.1	418	15.8	6.7	32.8	1.33	0.53	1.4×10^5
	26-Aug-04	9.4	359	14.4	6.9	23.2	0.94	1.15	6.7×10^5
Bore 1 (12-18 h) (diesel + gas.)	30-Aug-04	8.4	477	34.4	20.5	12.2	1.69	0.59	6.4×10^5
	31-Aug-04	7.4	527	36.2	29.1	9.9	3.65	0.62	3.9×10^5
	1-Sep-05	9.4	499	37.2	28.2	15.4	2.84	0.55	7.4×10^5
	2-Sep-05	9.9	498	41.1	33.4	17.6	1.91	0.52	7.8×10^5

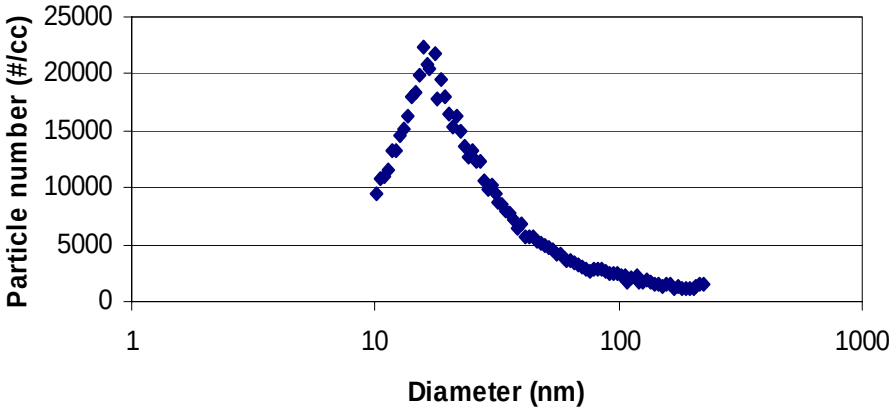
Pollutant Concentrations

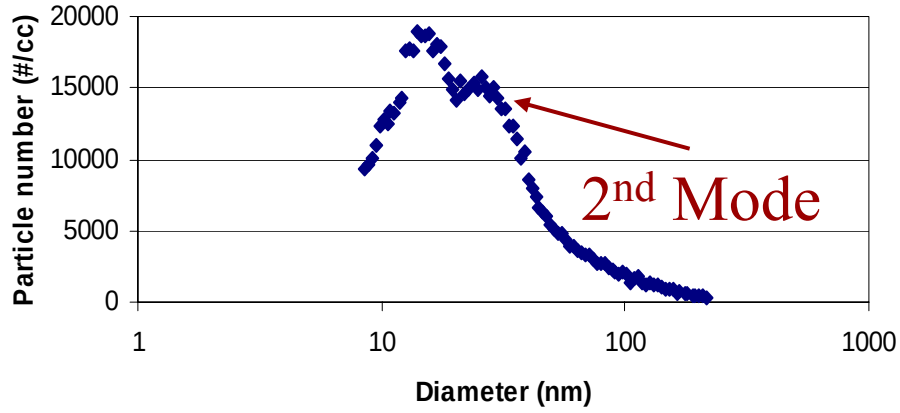
- Bore 1 concentrations higher than Bore 2
  - PM10 = 2.3 times
  - EC = 4 times
  - Sulfate = 2.5 times
- PN about 25% higher in Bore 1
- CO and CO_2 concentrations similar for both bores

Particle Size Distributions

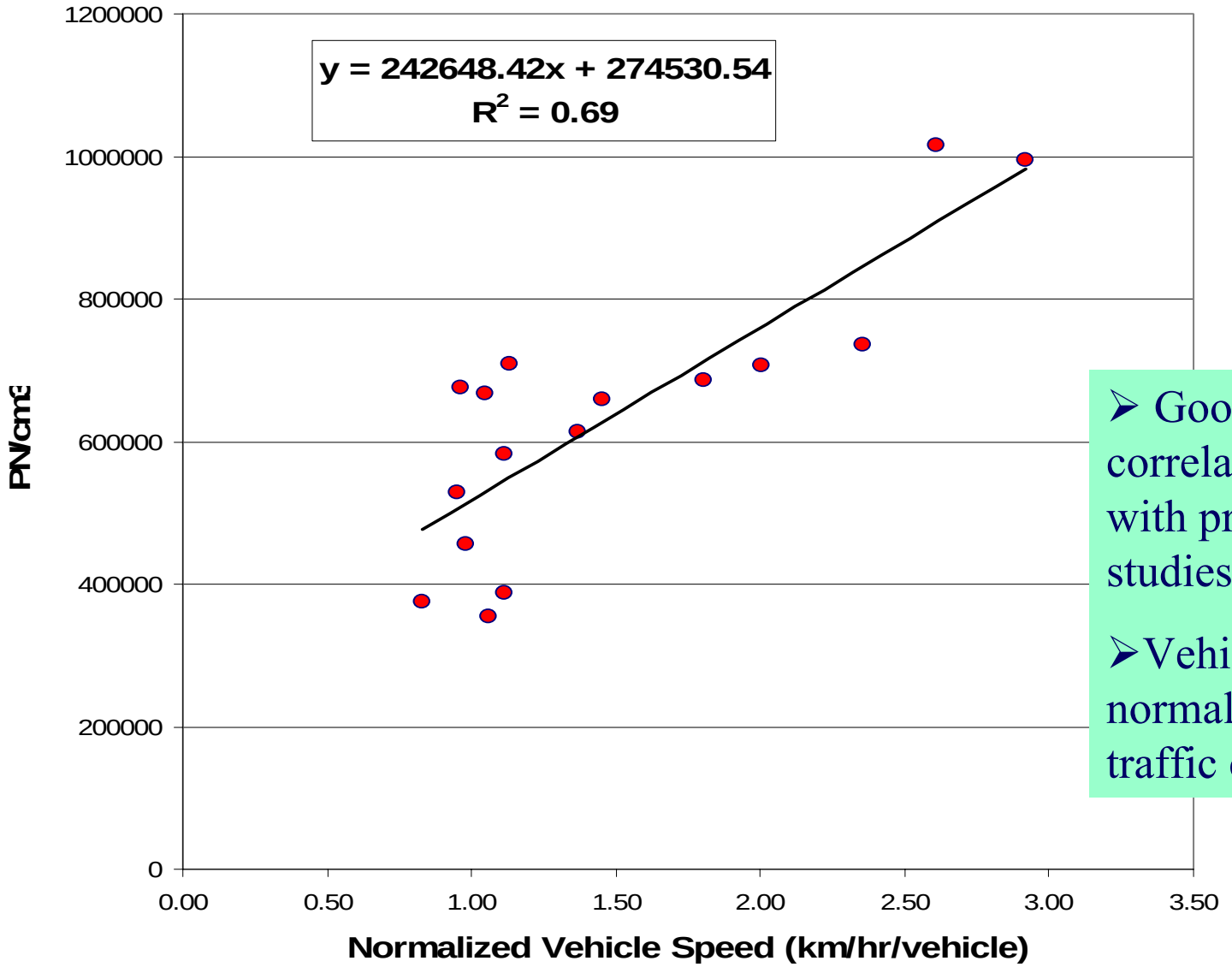








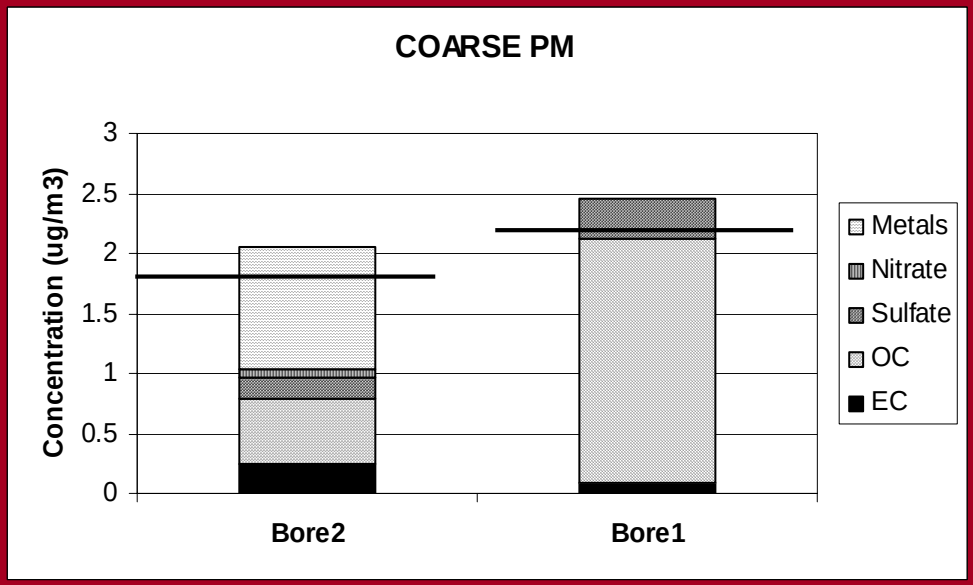
Effect of Vehicle Speed

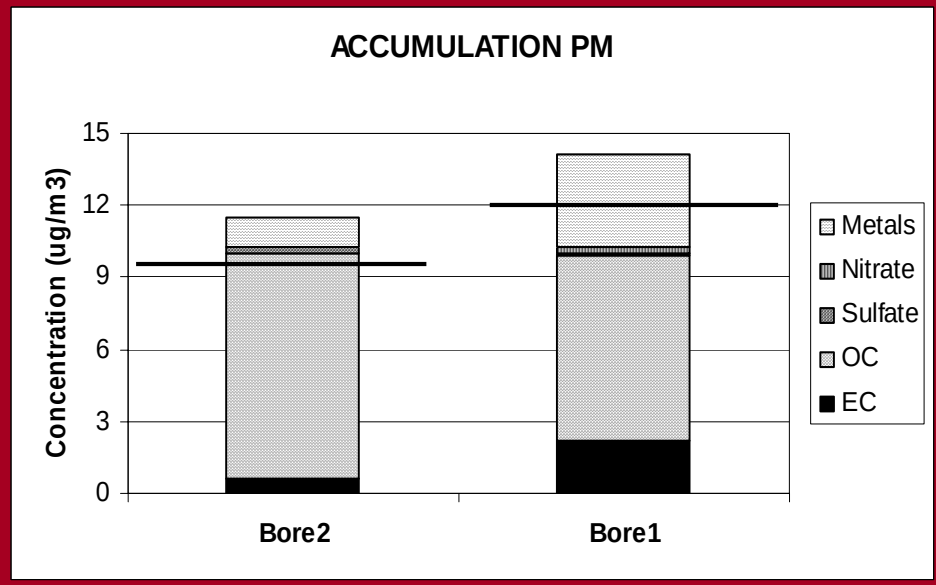


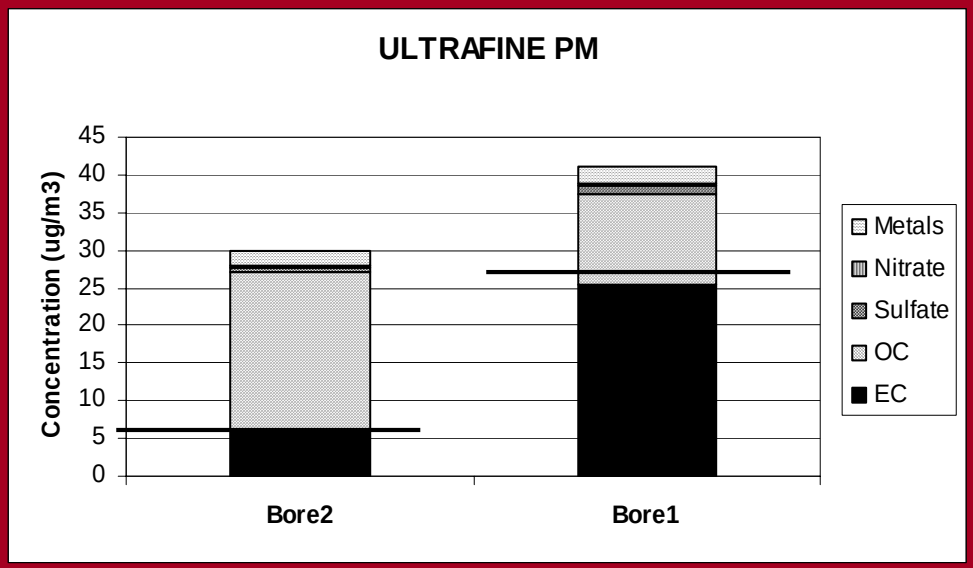
$R^2 = 0.69$

- Good correlation, agrees with previous studies
- Vehicle speed normalized to traffic counts

Mass Balance



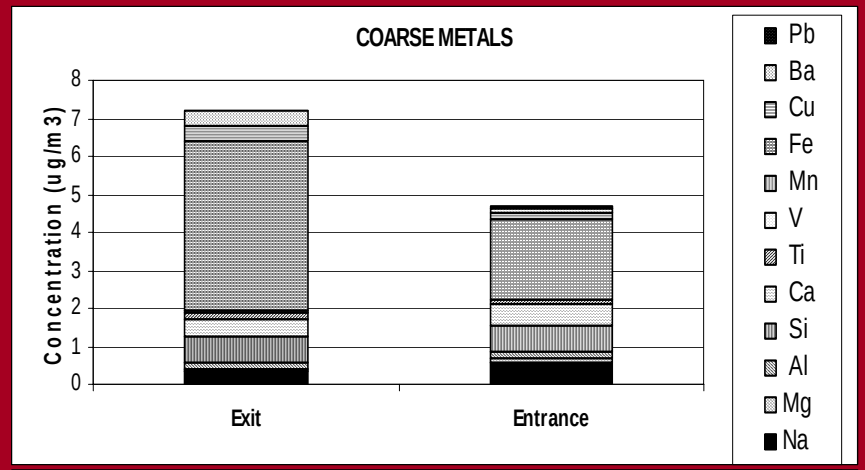


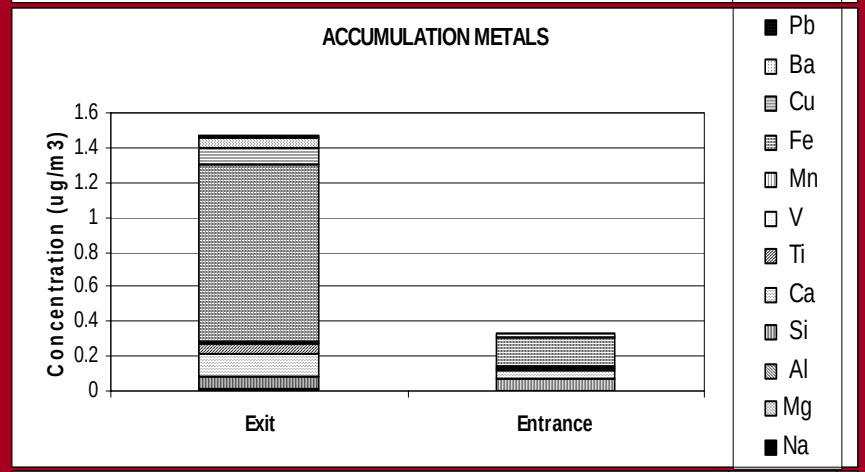


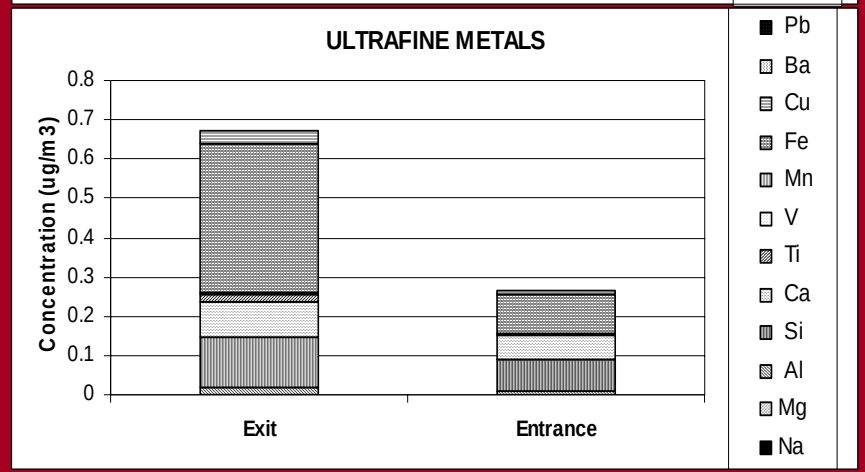
- Sum of chemical species consistent with weighed mass for >0.15 um
- Exception: UF fraction due to vapor adsorption but also filter losses
- OC often dominates all PM ranges
- Mass mostly in UF mode

Bore 2 Metals

- Exit concentrations are higher than entrance concentrations for each size fraction
- Most metals in coarse PM fraction
- Most abundant metal is iron
- Al-Si ratios similar for coarse and accumulation mode PM at entrance and exit

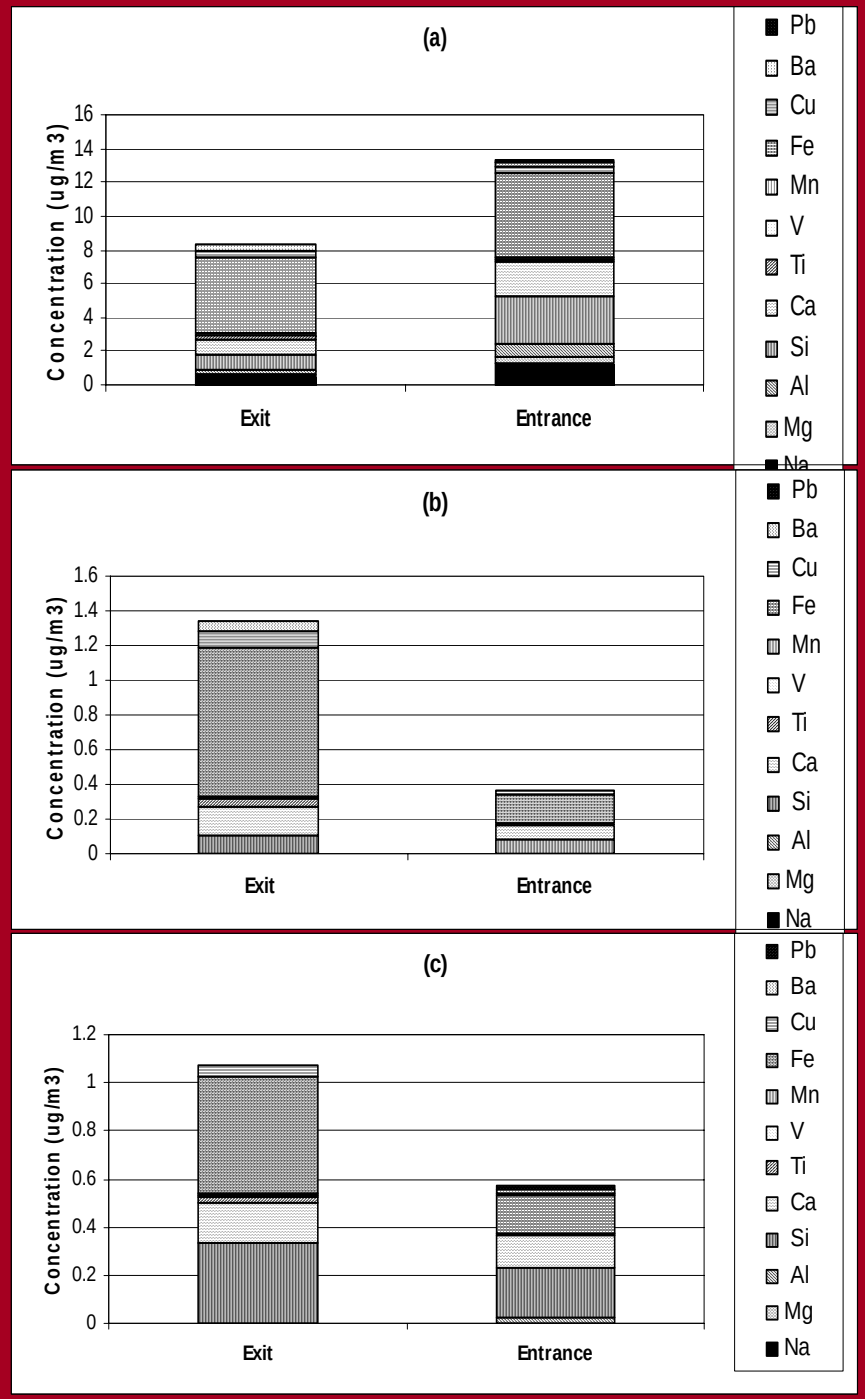






Bore 1 Metals

- Exit concentrations are higher than entrance concentrations for accumulation and ultrafine fractions but not coarse fraction
- Majority of metal mass is iron
- Silicon is present in much higher proportion in bore 1 UF
- Bore 1 acts as a “sink” for coarse PM



Coarse PM Generation a Function of Traffic Flow?

Hypothesis:

1. Road dust deposited at east end of bore 2 is resuspended when vehicles exit the tunnel
2. Since Bore 1 has only one traffic direction, road dust does not build up as heavily at the east end

Emission Factor Calculations

$$E_p = 10^3 \left(\frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \right) w_c \qquad (1)$$

$$\frac{\Delta[CO_2]_D}{\Delta[CO_2]} = \frac{f_D U_D \rho_D w_D}{f_D U_D \rho_D w_D + (1 - f_D) U_G \rho_G w_G} \qquad (2)$$

$$\Delta[P]_D = \Delta[P] - \Delta[CO] \cdot (1 - f_D) \cdot \left(\frac{\Delta[P]_2}{\Delta[CO]_2} \right) \qquad (3)$$

w_e is the weight fraction of carbon in fuel , Δ[CO2]D is the component of D [CO2] attributable to heavy-duty diesel emissions, f_D is the fraction of traffic identified as heavy-duty diesel trucks, U is the fuel consumption rate (reciprocal of fuel economy), ρ is fuel density, D and G are diesel and gasoline, respectively

Emission factors were computed as described by Kirchstetter et al. (1999)

Emissions are apportioned between diesel and gasoline vehicles in the mixed bore by using the data from the gasoline bore.

Emission factors are expressed in terms of mass or number emitted per kg fuel burned using the CO2 and CO measurements to determine fuel consumption.

Table 3. Average properties of diesel and gasoline fuel

Parameter	Fuel Type	
	Diesel	Gasoline
Carbon Weight Fraction, W_c	0.87	0.85
Density (g/l)	840	740
Sulfur (ppm by weight)	135	12
Fuel Consumption (l/100km)	47	12

Size-Segregated PN Emission Factors

Light-Duty Vehicles

Day	10-18 nm	18-32 nm	32-56 nm	56-100 nm	100-180 nm	>180 nm	Total
1	1.3E+15	6.5E+14	2.4E+14	1.3E+14	5.6E+13	5.9E+12	2.3E+15
2	1.9E+15	1.1E+15	3.7E+14	1.6E+14	6.7E+13	8.0E+12	3.6E+15
3	2.5E+14	2.1E+14	6.6E+13	3.4E+13	1.5E+13	2.2E+12	5.8E+14
4	8.3E+14	1.5E+15	6.3E+14	3.1E+14	1.3E+14	1.7E+13	3.4E+15
Grand Average	**1.1E+15**	**8.6E+14**	**3.3E+14**	**1.6E+14**	**6.7E+13**	**8.2E+12**	**2.5E+15**
Std dev	**7.0E+14**	**5.4E+14**	**2.4E+14**	**1.1E+14**	**4.8E+13**	**6.2E+12**	**1.4E+15**

Heavy-Duty Diesel Vehicles

Day	10-18 nm	18-32 nm	32-56 nm	56-100 nm	100-180 nm	>180 nm	Total
1	4.3E+15	1.6E+15	4.8E+14	3.3E+14	2.0E+14	9.3E+13	7.0E+15
2	4.9E+15	3.6E+15	1.4E+15	7.7E+14	4.2E+14	7.4E+13	1.1E+16
3	3.7E+15	1.1E+15	7.5E+14	4.7E+14	3.7E+14	6.0E+13	6.5E+15
Grand Average	**4.3E+15**	**2.1E+15**	**8.8E+14**	**5.2E+14**	**3.3E+14**	**7.5E+13**	**8.2E+15**
Std dev	**5.5E+14**	**1.3E+15**	**4.9E+14**	**2.3E+14**	**1.2E+14**	**1.7E+13**	**2.5E+15**

- HDVs emit more particles in every size range
- Ratio of HDV-to-LDV emission factors increases with particle size range
  - HDVs emit more fractal-like soot agglomerates

Table 7. Comparison of the current measured concentrations of CO_2 and emission factors of $PM_{2.5}$ and PN to measurements made in previous studies at the Caldecott tunnel.

Vehicle Type	Study	CO_2 (ppm)	$PM_{2.5}$ (g/kg)	Particle Number (#/kg)
LDV	USC (current)	384	0.07 ± 0.02	$(2.5 \pm 1.4) \times 10^{15}$
LDV	Kirchstetter (1997)	665	0.11 ± 0.01	$(4.6 \pm 0.7) \times 10^{14}$
LDV	Allen (1997)	738.5	0.07 ± 0.05*	n/a
HDV	USC (current)	515	1.02 ± 0.04	$(8.2 \pm 2.5) \times 10^{15}$
HDV	Kirchstetter (1997)	373	2.5 ± 0.2	$(6.3 \pm 1.9) \times 10^{15}$
HDV	Allen (1997)	435.5	1.285 ± 0.2*	n/a

*represents $PM_{1.9}$

- $PM_{2.5}$ emissions have declined by 37% (LDV) and 60 % (HDV) since 1997
- PN emissions have increased
  - Factor of 5.4 for LDV
  - Factor of 1.4 for HDV

Light-duty vehicle and heavy-duty diesel emission factors in mg kg-1 of fuel burned (average ± SD).

Light-duty	Mode		
	Coarse (2.5 – 10 μm)	Accumulation (0.18 – 2.5 μm)	Ultrafine (< 0.18 μm)
Mass	7.7 ± 1.6	40 ± 8	27.1 ± 3.2
OC	2.4 ± 0.9	7.4 ± 2.3	**
EC	1.0 ± 0.6	2.6 ± 1.2	26.8 ± 3.1
Nitrate	0.6 ± 0.3	0.42 ± 0.2	1.2 ± 0.9
Sulfate	0.8 ± 0.4	1.1 ± 0.9	2.7 ± 1.8
Mg	0.4 ± 0.2	0 ± 0	0 ± 0
Al	0.2 ± 0.4	0 ± 0	0.1 ± 0.1
Si	1.6 ± 1.3	0.1 ± 0.1	0.3 ± 0.1
Ca	0.8 ± 0.3	0.4 ± 0.2	0.3 ± 0.0
Fe	10.4 ± 3.1	3.7 ± 0.9	1.23 ± 0.50
Ti	0.3 ± 0.2	0.2 ± 0.1	0.1 ± 0.0
Ba	1.2 ± 0.9	0.3 ± 0.2	0 ± 0

Heavy-duty	Mode		
	Coarse (2.5 – 10 μm)	Accumulation (0.18 – 2.5 μm)	Ultrafine (< 0.18 μm)
Mass	75 ± 15	304 ± 62	711 ± 65
OC	12.3 ± 2.6	19.0 ± 5.6	**
EC	66 ± 17	306 ± 44	403 ± 32
Nitrate	0.4 ± 0.0	4.5 ± 1.0	1.8 ± 0.9
Sulfate	1.9 ± 0.5	10.7 ± 0.4	37 ± 9
Mg	-8.2 ± 6.3	0.0 ± 0.0	0.0 ± 0.0
Al	-12.2 ± 1.9	0.0 ± 0.0	0.6 ± 0.2
Si	-51 ± 44	0.6 ± 0.1	0.6 ± 0.3
Ca	-30 ± 9	0.3 ± 0.1	0.2 ± 0.1
Fe	-154 ± 58	4.3 ± 2.0	2.8 ± 0.9
Ti	-3.3 ± 1.7	1.3 ± 0.2	0.8 ± 0.1
Ba	-15.2 ± 3.5	0.9 ± 0.1	0.0 ± 0.0

** not presented due to substantial organic adsorption artifact

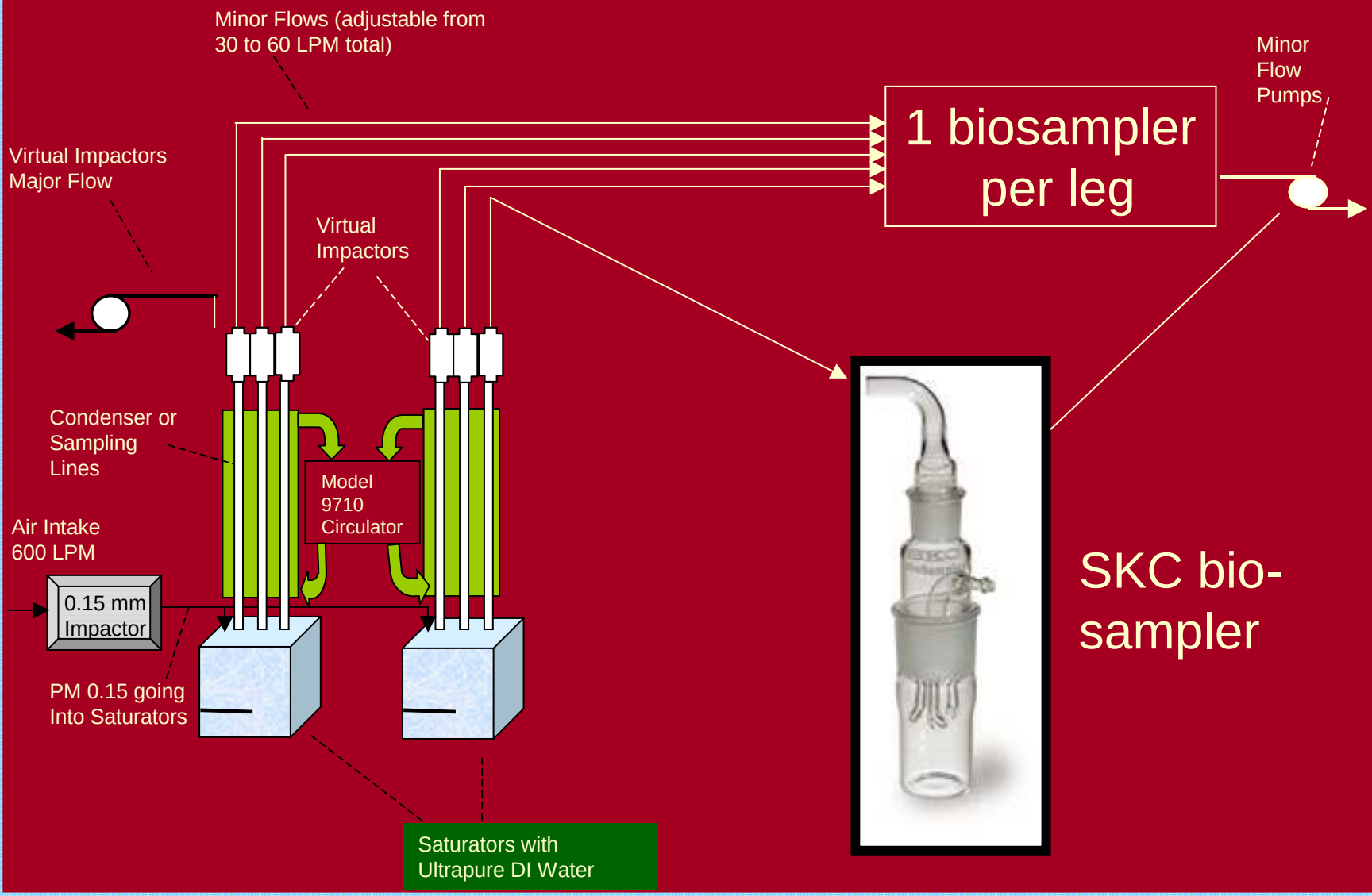
Toxicological Bioassays of Size Fractionated PM in the Two Bores

The central hypothesis is that many adverse health effects associated with PM exposure derive from oxidative stress, initiated by the formation of reactive oxygen species (ROS) in affected cells

The term “oxidative stress” refers an imbalance between pro-oxidants and antioxidant protection.

Work from our center and many other research groups implicates oxidative stress in pro-inflammatory effects in the nose, lung, and cardiovascular system

In Vitro PM Collection with Concentrator



Two Different Bioassays Tested:

DTT assay (Li et al, 2003; Cho et al, 2005):

We examined the redox properties of PM using their ability to catalyze electron transfer from dithiothreitol (DTT) to oxygen

Rate of redox cycling expressed as nmoles DTT consumed per minute per µg of particle suspension sample.

Ascorbate Depletion Assay (Zielinski et al, 1999, Mudway et al, 2001)

Lung lining fluid contains a range of low molecular weight antioxidants

Ascorbate is a reducing agent and scavenges a variety of free radicals in vitro including ROS.

Ascorbate looses one-electron resulting in the formation of the semi-dehydroascorbate radical which is subsequently transformed to dehydroascorbate and oxidized glutathione. This reaction is the basis for the ascorbate depletion assay which can be used as a biologically-based measure of redox activity.

Results from Bioassay Tests

Size and Bore	C1	F+UF1	UF1	C2	F+UF2	UF2
DTT (nmoles/ug of PM/min)	0.019	0.068	0.111	0.032	0.075	0.172
ASC (nmoles/ug of PM/min)	0.051	0.041	0.117	0.061	0.081	0.115

- C: coarse (2.5-10 um); F+UF: fine (0-2.5 um); UF : ultrafine (<0.15 um) particles.

- Higher activity in UF PM in both bores

- UF in Bore 2 most active

Results from Bioassay Tests By Vehicle Type and Size Range

Size and Bore	F+UF HDV	UF HDV	F+UF LDV	UF LDV
DTT (nmoles/ug of PM/min)	0.061	0.072	0.075	0.172
ASC (nmoles/ug of PM/min)	0.023	0.118	0.081	0.115

- UF PM in LDV as active (based on ascorbate) or more active (based on DTT) on a per mass basis than any other particle range

Concluding Remarks:

- LDV PM2.5 emissions have dropped by 37%, and HDV PM2.5 emissions have declined 60% in the past seven years.

- Fuel efficiency and increased use of more-efficient diesel engine emissions controls, which have become more prevalent due to regulations on diesel truck emissions, may be a likely cause

- Since 1997 LDV particle number emission rates have increased by a factor of 5.4 and HDVs by 1.3.

- Older engines emit higher concentrations of carbonaceous material, offering a large surface area for adsorption of condensable volatile compounds, a process that counteracts the formation of smaller particles by nucleation.

- As the emissions of carbonaceous PM of newer engines decreases, the formation of nucleation mode particles may be favored due to the reduction of the available surface for adsorption of the semi-volatile material.

- The resulting supersaturation of the mostly organic vapor increases the production of nano-particles by nucleation

• Nucleation may become especially strong if catalytic after-treatment devices (catalytic traps or catalytic converters) are applied (Vaaraslahti,et al, ES&T, 2004; Holmen and Ayala, ES&T, 2002).

•The semi-volatile PM fraction of vehicle emissions may be extremely important in terms of its contributions to human exposure (freeway or roadway proximity)

• To-date, there is no information on the relative toxicity of these particles compared to the larger, non-volatile (refractory), mostly carbonaceous fraction. Such data are greatly needed.

Study Sponsors:

- **California Air Resources Board**

- **Southern California Particle Center and Supersite funded by US EPA STAR Program**