

# **Tire Wear Emissions for Asphalt Rubber and Portland Cement Concrete Pavement Surfaces**

**Arizona Department of Transportation  
Contract KR-04-0720-TRN**

**Final Report  
April 2006**

**Submitted by**

**Jonathan O. Allen, Ph.D., P.E.  
Olga Alexandrova, Ph.D.  
Department of Chemical & Materials Engineering**

**Kamil E. Kaloush, Ph.D., P.E.  
Department of Civil & Environmental Engineering  
Ira A. Fulton School of Engineering  
Arizona State University  
Tempe, AZ 85287-5306**



## Table of Contents

1	Introduction.....	2
2	Objectives .....	3
3	Methods.....	3
3.1	Tunnel Sampling.....	3
3.2	Analysis of Tire Wear Markers in Crumb Rubber Material .....	5
3.3	Analysis of Tire Wear Markers in Tire Tread Samples .....	6
3.4	Analysis of Tire Wear Markers in Aerosol Samples .....	9
4	Results and Discussion .....	9
4.1	Tunnel Traffic .....	9
4.2	Aerosol Concentrations.....	12
4.2.1	Tire Marker Compounds.....	<b>12</b>
4.2.2	Tire Wear Emission Rate .....	18
4.2.3	Tire Wear Emission Rates Based on Tire Wear Tracers .....	18
4.2.4	Polycyclic Aromatic Hydrocarbons in the Deck Park tunnel .....	19
4.3	Roadway Characteristics.....	22
4.3.1	Roughness Measurements.....	22
4.3.2	Friction Measurements.....	24
4.3.3	Pavement Temperature .....	25
5	Conclusions.....	26
6	Acknowledgements.....	27
7	References.....	27

## 1 Introduction

Since 1990, it has been the policy of the State of Arizona that the recycling and reuse of waste tires are the highest priority. The Arizona Department of Transportation (ADOT) has long supported the use of recycled waste tire rubber in asphalt rubber hot mix. AR mixtures have been shown to perform successfully and have several added benefits such as the reduction of highway noise, providing better surface drainage characteristics to enhance visibility and skid on wet pavement surfaces. Furthermore, some aspects of life cycle costs have also been conducted and demonstrated the potential impacts on maintenance and rehabilitation savings to ADOT. Joint ASU/ADOT research activities related to Asphalt Rubber (AR) mixtures started in July 2001 and are continuing. In this work we test the hypothesis that AR-ACFC road surface layer results in less tire wear than PCC road surface layer.

Tire wear contributes to atmospheric particulate matter (PM) which is regulated by the United States Environmental Protection Agency (US EPA) because PM has been shown to affect human health. PM is classified by the size of the particles; PM<sub>10</sub> and PM<sub>2.5</sub> include particles with diameters smaller than 10 and 2.5  $\mu\text{m}$ , respectively. PM<sub>2.5</sub> has been shown to contribute to morbidity and mortality (Dockery et al., 1993; Pope et al., 1995; Katsouyanni et al., 1997; Krewski et al., 2000). This epidemiological research has found consistent and coherent associations between outdoor air quality and health outcomes including respiratory symptoms, reduced lung function, chronic bronchitis, and mortality (Bates, 1992). The PM<sub>10</sub> fraction includes particles that are respirable, and so of concern for human exposure.

Vehicle emissions are a significant source of both PM<sub>2.5</sub> and PM<sub>10</sub>. Vehicle fleet emissions per mile traveled have been reduced significantly in the last 30 years as a result of improved engine operation and tailpipe controls; this downward trend is expected to continue into the future and is an important means to reduce PM. The main focus of these reductions has been on tailpipe emissions; however, “zero emission” vehicles will continue to generate PM from tire wear, road wear, brake wear, and re-suspended road dust. These non-tailpipe emissions will become a relatively more important component of PM emissions but are difficult to characterize. In this proposal work, we apply our existing aerosol measurement expertise (Allen et al., 1996; Allen et al., 2001) to evaluate tire wear emissions from the vehicle fleet using the Deck Park highway tunnel in Phoenix, AZ.

The amount of rubber loss was estimated to average approximately 90 mg/km (Dannis, 1974) which corresponds to 1.3 million metric tons per year for the entire US (Reddy and Quinn, 1997). Tire wear particles are generated during rolling shear of the tire tread against the road surface. Average tire tread wear rate for single passenger tire is between 6 and 900 mg/km, depending on the road surface type (e.g., asphalt vs. concrete), driving conditions (acceleration, abrupt deceleration, speeding, etc) and tire conditions (tire pressure, vehicle load, retread vs. new, etc.). Tire wear emissions (TIRE) are estimated in the EPA MOBILE 6.1 model as:

$$\text{TIRE} = 0.002 * \text{PSTIRE} * \text{WHEELS}$$

where TIRE has units g/mi, PSTIRE is the fraction of particles smaller than a cutoff size, and WHEELS is the number of wheels on a vehicle (EPA, 2003). For PM<sub>10</sub>, PSTIRE is 1.0; for PM<sub>0.1</sub>, PSTIRE is 0.01. Using this formula, a passenger vehicle is estimated to emit 13 mg/km of PM<sub>10</sub> and 0.13 mg/km PM<sub>0.1</sub>. The MOBILE 6.1 emission estimates are used for air quality modeling, however these factors have not been verified experimentally for existing or new pavement surfaces.

We hypothesize that AR-ACFC road surface layer results in significantly less tire wear than PCC road surface layer. Reduced tire wear would result in lower vehicle operating costs and lower particulate matter (PM) emissions from vehicle traffic. In the present research, we measured the rate tire-wear marker compounds in PM emissions at the Deck Park Tunnel Highway on Interstate 10. The Deck Park Tunnel highway surface was PCC until June, 2004, when it was resurfaced with an AR-ACFC. This research takes advantage of a rare opportunity to sample tire wear emissions at the tunnel before and after the AR-ACFC overlay.

Measured tire wear emission rates developed here may then be used by ADOT as inputs to federally-mandated air quality models for the Phoenix airshed. If, as hypothesized, resurfacing with the AR-ACFC reduces tire wear emissions, this additional benefit of AR may be incorporated in ADOT air quality planning.

## 2 Objectives

The objectives of this study are:

1. Measure the PM emissions from the on-road vehicle traffic during typical highway driving conditions for two different roadway surfaces: AR-ACFC and PCC.
2. Analyze PM emissions to determine emission factors for tire wear emissions for the two different road surface types. Evaluate the hypothesis that AR-ACFC road surface results in significantly less tire wear emissions than a PCC surface.
3. Collect and analyze representative tire tread samples for tires wear marker compounds including 24MoBT (2-(4-morpholinyl) benzothiazole) and NCBA (N-cyclohexyl-2-benzothiazolamine). Test extraction and separation protocols to determine the amount of 24MoBT and NCBA in tire treads.
4. Report along with the tire wear emissions the roughness and frictional characteristics of the two pavement types.

## 3 Methods

### 3.1 Tunnel Sampling

Drs. Allen and Kaloush conducted a site visit to the tunnel in April 2004 guided by Mr. George Way and Edward Walsh of ADOT. The experimental design is based on that site

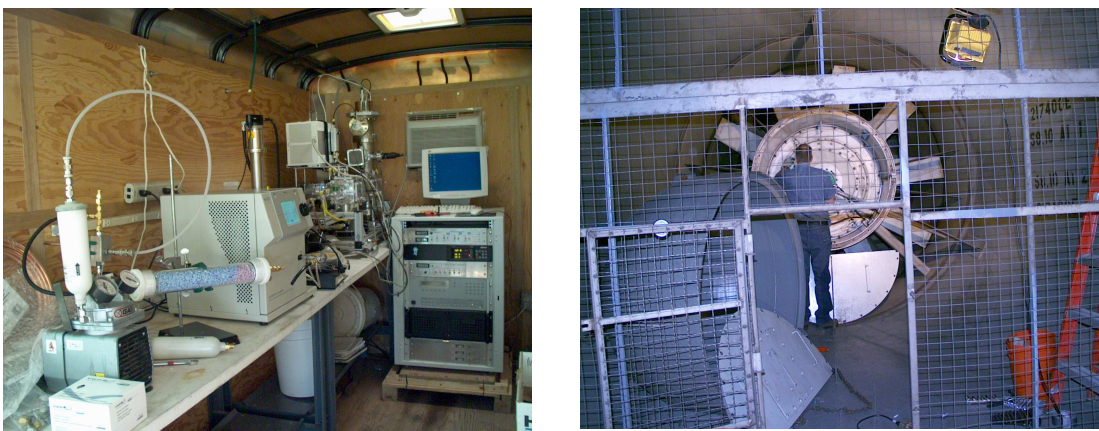
visit and the results of experiments at the Deck Park tunnel in January and July 1995 (Gertler et al., 1997).

Gertler and coworkers determined emissions of gas-phase pollutants from the Phoenix vehicle fleet based on measurements of pollutant concentrations the tunnel inlet and outlet. They found that pollutants in the tunnel were poorly mixed with concentrations of pollutants away from the HOV lane was ~1.5 higher than that near the HOV lane. Poor mixing was attributed to the Deck Park tunnel width, 217 m<sup>2</sup> cross section at its narrowest point. Reliable determination of emission factors from tunnel measurements requires uniform concentrations at the exhaust sampling point.

In this experiment, the existing forced ventilation system was used to mix the vehicle emissions in the tunnel. During the experiments exhaust fans in the second half of the tunnel were run in high-flow exhaust mode. Sampling instruments were positioned at the tunnel entrance and at the tunnel exhaust chimney (see Figures 1 and 2 below).



**Figure 1: Sampling sites from the May 2004 experiment. Aerosol measurements were made next to entrance of westbound tunnel (left photo) and from the exhaust chimney for the western half of the westbound tunnel (right photo).**



**Figure 2: Aerosol sampling equipment (left photo, inside trailer) and the exhaust fan during maintenance (right photo).**

Tunnel experiments have been performed on 27-28 May 2004 before the highway was resurfaced and were performed again in June 9-10, 2005 (see Table 1). Vehicle emissions were sampled during rush hour (07:00-09:00) and midday (10:00-14:00) in order to measure emissions from the mainly light-duty vehicle fleet during rush hour and the mixed light- and heavy-duty fleet later in the day. In normal tunnel operation, the exhaust fans are turned off at these times.

**Table 1. Deck Park Tunnel Experiments.**

No.	Date	Start	End
PCC road surface			
1	Thu 27 May 2004	10:00	14:00
2	Fri 28 May 2004	07:05	09:05
3	Fri 28 May 2004	10:00	14:00
AR-ACFC road surface			
4	Thu 09 Jun 2005	07:00	14:00
6	Fri 10 Jun 2005	07:00	14:00

Particulate pollutant concentrations in the tunnel bores were measured using two high volume cascade impactors, ChemVol 2400 (Rupprecht & Pataschnick, Albany, NY). One impactor was positioned to sample incoming air at the eastern entrance of the tunnel; the second at the western exit of the tunnel.

CO<sub>2</sub> concentrations were measured at the tunnel exhaust chimney using a LiCor 7500 (Lincoln, NE) infrared hygrometer.

A sample of vehicles were counted and identified by type from a video camera at the exit of the westbound tunnel. From these data, we determined the number of passenger vehicles, medium duty truck, and heavy duty truck miles during each of the sampling periods.

### **3.2 Analysis of Tire Wear Markers in Crumb Rubber Material**

Crumb Rubber Material (CRM) samples were extracted to determine the concentration of tire wear markers in tires currently used in the US. Three CRM samples were represented by mixture of old recycled tires (both mixtures of different manufacturers), and the new defective Firestone tires (from the ADOT - Ford Motor Company demonstration study). These samples were collected from projects that were completed in the State of Arizona. All three samples were sieved to select particles less than 150 µm.

Each tire wear sample was spiked prior to extraction with known amount of mixture of perdeuterated standard mixture. Tire wear samples were extracted twice with isopropanol, followed by three successive extractions with dichloromethane. Extracts were combined and filtrated through a pre-cleaned glass wool. Extracts were purified using column chromatography according to the procedure used by Kumata et al., 1996.

### 3.3 Analysis of Tire Wear Markers in Tire Tread Samples

To analyze a representative sample of tread from used tires in Arizona tire tread samples were collected from the Queen Creek Crumb Rubber Recycling plant. Fragments of tire wear (approximately 0.5 x 0.5 x 4 cm) were cut out of the surface of 15 heavy duty and 15 light duty tires of different brands as shown in Tables 2 and 3, respectively. (see Figure 3).

Tire wear fragments were composited to two samples, heavy duty and light duty. Both samples were ground using the blender (Model 51BL32, Waring Commercial) and sieved to select particles less than 150  $\mu\text{m}$ .

Tire wear composite samples were extracted to determine the concentration of markers mentioned above and to search for additional tire wear markers in tires currently used in the US. Each tire wear extract was spiked with known amount of mixture of perdeuterated standard mixture. Tire wear samples were extracted twice with isopropanol, followed by three successive extractions with dichloromethane. Extracts of heavy duty and light duty tire wear composites were combined, filtrated through PTFE syringe filters (Acrodisc CR 25mm Syringe Filters, PALL Life Science), and evaporated to 24.8ml and 20.0ml respectively. The concentrations of tire wear tracer compounds were measured using Hewlett Packard GC/MS - Agilent 6890 with Agilent 5973 inert Mass Selective Detector. Organic compounds were identified by comparison with reference standards and NIST mass spectral library.



**Figure 3: Tire tread samples collected from the Queen Creek Crumb Rubber Recycling plant.**

**Table 2: Tire Tread Samples Used for Heavy Duty Composite.**

#	Manufacturer, model	Notes
1	Bridgestone R294 255/70 R 22.5 Low Profile Radial Original Tread	Side wall failure visible
2	Bridgestone R194 295/75 R 22.5 Low Profile Radial Re-tread	
3	Good Year 11R22.5 Radial Unisteel II Regroovable Tread 5Plies Steel Cord, side wall 1 Ply steel cord	
4	Armorsteel Kelly/KDA, Regroovable, 11 R 22.5 Radial That 5 Plies Steelcord, silwall 1 ply steel cord Max load snlge 6175 lbs at 105psi cold Max load dual 6750 lbs at 105psi cold	
5	Good Year 6314 Unisteel negroovable 11 R 22.5 Radial	Side wall puncture
6	Michelin 275/80 R22.5 16PR T575LP Radial	Side wall damage
7	Firestone 255/70R 22.5 16PR T 575LP Radial	Side wall damage
8	Armstrong SD-300 E/S 11-22.5 Tubeless, regroovable	Side wall damage/puncture
9	Yokohama 11 R22.5 14 PR Snow Super steel TY 287 Stem (Japan)	
10	Firestone T559 Radial, tubeless, regroovable, 11R 22.5 14 PR	
11	Dunlop SP 131 11R 22.5 RK 891 A, regroovable, 5 ply tread, 1 ply silwall	
12	Yokahama Super steel RY 112A, 11R24.5, retread (USA)	side wall fracture
13	Michelin 275/80 R22.5 XDA2 Re-tread	
14	Good Year Regional RHS, 315/80R22.5, ECD	blow out
15	General D450, Continental 11R22.5	



**Table 3: Tire Wear Samples used for Light Duty Composite**

#	Manufacturer, model	Notes
1	(SUV) Michelin P235/65R17, 103SM+S, tubeless, radial LTX A/S	worn
2	(SUV) BF Goodrich, Radial Long Trail T/A, P235/70R16, 1045 M+S tubeless, radial	This sample was harder than #1 to collect; some nails in the tire
3	(SUV) Big Foot, B13 A/T, M+S LT 235/85R16, 120/116P, Max load range 1380kg single/1250kg dual 80psi cold	side damage; tough to sample
4	(SUV Jeep) Good year, Wranger, MT/R, Dura wall, puncture resistance technology LT245/75R16, 120/116P	worn on one side
5	BF Goodrich, TouringT/A, 205/70R15, All seam (tough- semi/medium)	
6	BF Goodrich, Precept Touring, P205/70R15 95S M+S (soft)	side damage
7	Dunlop, SP Sport 270(wide tire), p225/55R17 95H	worn
8	Cornell 535, P175/80R13, All seam radial	worn on one side
9	Bridgestone, Duelev H/T 687, 215/70R16, 995	
10	Goodyear Eagle GA P225/60R16	worn
11	WANAL S-1099 205/40 Z R17 80W	nail puncture
12	Goodyear Eagle GPS P225/60R16 97T	tread wear severely damaged on one side
13	Michelin XW4, P215/70R 15 97S wear	tough to collect
14	Nan Kay 195/70R 14 91H (Taiwan)	
15	General Touring A/S P185/65R14 85S wear	soft

### 3.4 Analysis of Tire Wear Markers in Aerosol Samples

Aerosol samples were collected using a high volume cascade impactor, the ChemVol 2400 (Rupprecht and Patashnick (Albany, NY)) (Demokritou et al., 2002, Lee et al., 2005). Aerosol samples were stored in precleaned glass jars at  $-20^{\circ}\text{C}$  until analyzed. Four size-segregated aerosol samples were analyzed for the tunnel inflow and outflow for the experiments done with the PCC and AR-ACFC pavement surfaces. Samples were extracted using multiple sequential extractions in isopropanol and dichloromethane that has been shown to remove efficiently non-polar and polar compounds from the ChemVol substrates. Organic compounds were identified by comparison with reference standards and mass spectral libraries. We have also assembled an extensive library of reference standard materials, including the tire wear marker compounds 24MoBT and NCBA.

The concentrations of 24MoBT and NCBA were measured using same GC/MS instrument as for analysis of tire wear tracers in tire tread samples. We assumed that this sampling and analysis procedure allows to collect sample containing sufficient material for quantitative analysis of organic tracer compounds with concentrations of  $\sim 0.2\text{ ng/m}^3$ .

## 4 Results and Discussion

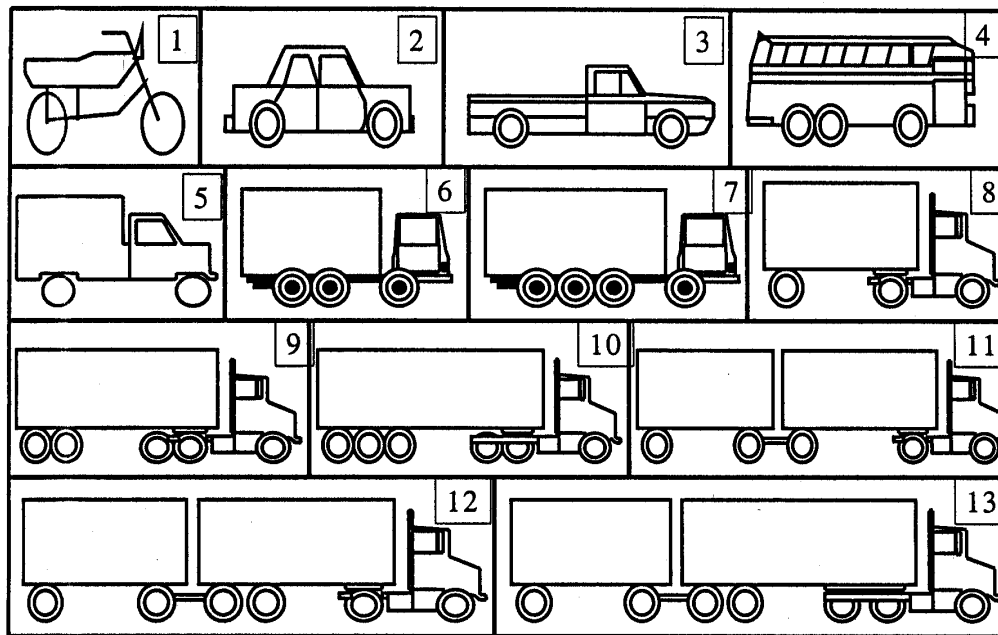
### 4.1 Tunnel Traffic

Traffic data was video-recorded (see Figure 4) on the I-10 west bound on may 27th and 28th 2004 and on June 9<sup>th</sup> and 10<sup>th</sup> 2005 corresponded with the sampling periods presented in Table 1. The total time recorded in 2004 was 10 hours. On may 27th, 4 hours of traffic were recorded from 10:00am-2:00pm and on may 28th, a total of 6 hours were recorded, from 7:00am-9:00am and from 10:00am-2:00pm.

In 2005 the total recorded time was 8 hours. On June 9<sup>th</sup> and 10<sup>th</sup>, 4 hours of traffic were recorded from 6:30 am to 2:30 pm, 15 minutes for every 30 minutes period. The total of vehicles grouped by different classification categories were obtained by manual counting using the tapes. The FHWA vehicle classification was used (see Figure 5). For simplicity, and for the purpose of this experiment, vehicle types 5, 6, 7 are counted together as group 5; vehicle types 8, 9 10 are counted together as group 6, and vehicles 11, 12 13 are counted as group 7.

**Figure 4: Video recording of traffic at the west bound tunnel exit.**





- |                                       |                                      |
|---------------------------------------|--------------------------------------|
| 1. Motorcycles                        | 2. Passenger Cars                    |
| 3. Two Axles, Four Tires Single units | 4. Buses                             |
| 5. Two Axles, Six tires Single Unit   | 6. Three Axle Single Units           |
| 7. Four or More Axle Single Units     | 8. Four or Less Axle Single Trailers |
| 9. Five Axle Single Trailers          | 10. Six or More Axle Single Trailers |
| 11. Five or Less Axle Multi-Trailers  | 12. Six Axle Multi-Trailers          |
| 13. Seven or More Axle Multi-Trailers |                                      |

**Figure 5: FHWA Vehicle Class Illustration and Definitions.**

Analysis of the data was conducted using the ten hours recorded on May 27-28 and the eight hours recorded on June 9-10.

For the analysis of the 2004 traffic, the first stage was based on the counting every five minutes for a period of three hours (three one hour interval). According to the data obtained, the traffic was fairly constant during each hour. Based on these results, the counting for the remaining intervals was performed at 5 minutes intervals for every 15 minutes period. Table 4 below provides a summary of the ten hours period counting.

For the analysis of the 2005 traffic, the analysis was based on the counting at 5 minutes intervals for every 15 minutes period. Table 5 summarized the 8 hours period counting.

**Table 4: Vehicle Counts May 2004****TOTAL NUMBERS OF VEHICLES**

DATE	TIME	VEHICLE TYPE							totals
		1	2	3	4	5*	6*	7*	
5/27/2004	10:00-11:00 AM	9	4417	1352	15	264	248	53	6359
5/27/2004	11:00-12:00 AM	13	4361	1320	13	291	231	0	6229
5/27/2004	12:00-1:00 PM	25	4673	1683	13	330	210	0	6934
5/27/2004	1:00-2:00 PM	19	5168	1767	43	288	204	0	7489
5/28/2004	7:00-8:00 AM	26	4431	1416	22	198	205	19	6317
5/28/2004	8:00-9:00 AM	33	5235	1469	32	194	172	9	7126
5/28/2004	10:00-11:00 AM	31	4736	1557	16	315	270	3	6928
5/28/2004	11:00-12:00 AM	40	4937	1617	7	291	201	0	7093
5/28/2004	12:00-1:00 PM	22	5429	1746	19	249	153	0	7618
5/28/2004	1:00-2:00 PM	16	5546	1767	22	249	183	0	7783
	<b>TOTAL VEHICLES</b>	<b>235</b>	<b>48935</b>	<b>15697</b>	<b>206</b>	<b>2669</b>	<b>2077</b>	<b>84</b>	<b>69903</b>

\* VEHICLE TYPE 5 CORRESPONDS TO TYPE 5, 6, 7 FROM FHWA

\* VEHICLE TYPE 6 CORRESPONDS TO TYPE 8,9,10 FROM FHWA

\* VEHICLE TYPE 7 CORRESPONDS TO TYPE 11,12,13 FROM FHWA

**Table 5: Vehicle Counts June 2005.****TOTAL NUMBERS OF VEHICLES**

DATE	TIME	VEHICLE TYPE							totals
		1	2	3	4	5*	6*	7*	
6/9/2005	6:30-7:30 AM	30	4182	1686	12	294	126	6	6336
6/9/2005	7:30-8:30 AM	30	4926	1614	0	192	144	0	6906
6/9/2005	8:30-9:30 AM	18	4650	1560	30	312	300	6	6876
6/9/2005	9:30-10:30 AM	18	3948	1620	6	300	324	12	6228
6/9/2005	10:30-11:30 AM	12	3948	1596	12	342	264	0	6174
6/9/2005	11:30-12:30 AM	30	4440	1914	12	306	294	6	7002
6/9/2005	12:30-1:30 PM	12	4674	2010	6	300	294	0	7296
6/9/2005	1:30-2:30 PM	12	5808	2448	30	366	306	6	8976
6/10/2005	6:30-7:30 AM	42	4278	1578	0	180	156	6	6240
6/10/2005	7:30-8:30 AM	18	4788	1638	30	198	162	6	6840
6/10/2005	8:30-9:30 AM	30	4518	1698	12	264	210	0	6732
6/10/2005	9:30-10:30 AM	12	4290	1722	6	252	276	6	6564
6/10/2005	10:30-11:30 AM	18	4482	1710	12	468	324	12	7026
6/10/2005	11:30-12:30 AM	24	3672	1482	18	330	168	6	5700
6/10/2005	12:30-1:30 PM	30	4974	2292	36	348	210	0	7890
6/10/2005	1:30-2:30 PM	18	5478	2262	6	324	252	12	8352
	<b>TOTAL VEHICLES</b>	<b>354</b>	<b>73056</b>	<b>28830</b>	<b>228</b>	<b>4776</b>	<b>3810</b>	<b>84</b>	<b>111138</b>
	<b>AVERAGE/HOUR</b>	<b>22</b>	<b>4566</b>	<b>1802</b>	<b>14</b>	<b>299</b>	<b>238</b>	<b>5</b>	<b>6946</b>

## 4.2 Aerosol Concentrations

### 4.2.1 Tire Marker Compounds

24MoBT concentrations found in CRM samples (Table 6) purified using column chromatography agree with the data obtained by Kumata et al., 1997 and Reddy and Quinn, 1997. Kumata et al. found a mean concentration of 2.3 ppm in particles generated mechanically of tire tread rubber from four different tires (Kumata et al., 1997). The concentration of 24MoBT in crumb rubber material was 3.8 ppm (Reddy and Quinn, 1997).

24MoBT and NCBA were identified in the samples of fine particulate matter collected in the Caldecott tunnel (California) in 1997 (Allen et al., 2001; Alexandrova and Allen, 2004). The emission rates of 24MoBT and NCBA per mass of carbon in fuel burned were calculated; this is a precise and directly measured emission rate, that can be scaled to an estimate of tire wear mass emission rates. Emission rates of 24MoBT (5.10  $\mu\text{g}/\text{kg}$  of C in fuel burned) and NCBA (1.11  $\mu\text{g}/\text{kgC}$ ) from the LDV fleet were higher than from the HDV fleet (2.90 and 0.80  $\mu\text{g}/\text{kgC}$ ). Higher benzothiazolamine emission rates for the LDV fleet relative to the HDV fleet is likely due to the different composition of automobile and truck tires (Kim et al., 1990). Note that identification of 24MoBT and NCBA in the samples collected at the Caldecott tunnel should be deemed as probable (Rogge et al., 1993) since authentic standard was not available to be run on the same GC/MS instrument as the samples were at that time.

The total amount of tire wear material can be calculated by multiplying the emission rate of tire wear markers 24MoBT and NCBA by the inverse fraction of these markers in whole tire treads. Although the calculated tire wear emission rate were greater than the *total* measured aerosol emission rate. We believe that the methods used by Reddy and Quinn, which were designed to measure the amount of tire wear markers which leach into water, underestimate by an order of magnitude the amount of 24MoBT and NCBA in tire tread. The method used by Kumata et al. includes extract cleaning procedure using column chromatography. Part of extract containing 24MoBT and NCBA can be lost during extract cleaning procedure what was confirmed by our experiment with 24MoBT standard solution applying the same procedure as Kumata et al. used.

**Table 6: 24MoBT concentrations found in crumb rubber samples purified using column chromatography.**

Sample	ng mg <sup>-1</sup>	Sample Description
CRM # 1	2.45	Used tires, mixture of different brands
CRM # 2	1.49	Used tires, mixture of different brands
CRM # 3	3.12	New Firestone tires (Ford Study)
<b>Average</b>	<b>2.35</b>	

Absence of authentic standard mentioned above can be also a part of the problem causing overestimated values of 24MoBT and NCBA emission rates.

24MoBT concentrations found in heavy duty and light duty composite samples are 9.62 ppm and 1.4 ppm respectively. Although no quantifiable amounts of 24MoBT were found in aerosol samples collected during both Deck Park tunnel experiments. Possibly automobiles driving through the tunnel at steady speed do not generate as much tire wear particles as under driving conditions which include breaking and stopping. Thus, the amount of aerosol material collected in the tunnel was not sufficient to get quantifiable 24MoBT concentrations. We assumed that tire wear may contain other organic compounds which can serve as tire wear tracers. Chromatograms of heavy and light duty tire wear composite extracts have been analyzed to determine such organic compounds. Three compounds with chemical structures showing presence of aromatic rings, nitrogen, and sulfur have been detected using NIST MS Search software. Figures 6 through 8 show the spectra of the compounds # 3, 4, 5 respectively from GRAMS. Concentrations of these compounds in light and heavy duty tire wear composites are shown in Table 7. Note that the concentrations of tire wear tracer compounds # 3 and 4 are 1.4-1.8 orders higher in heavy duty tire wear composite than in the light duty one.

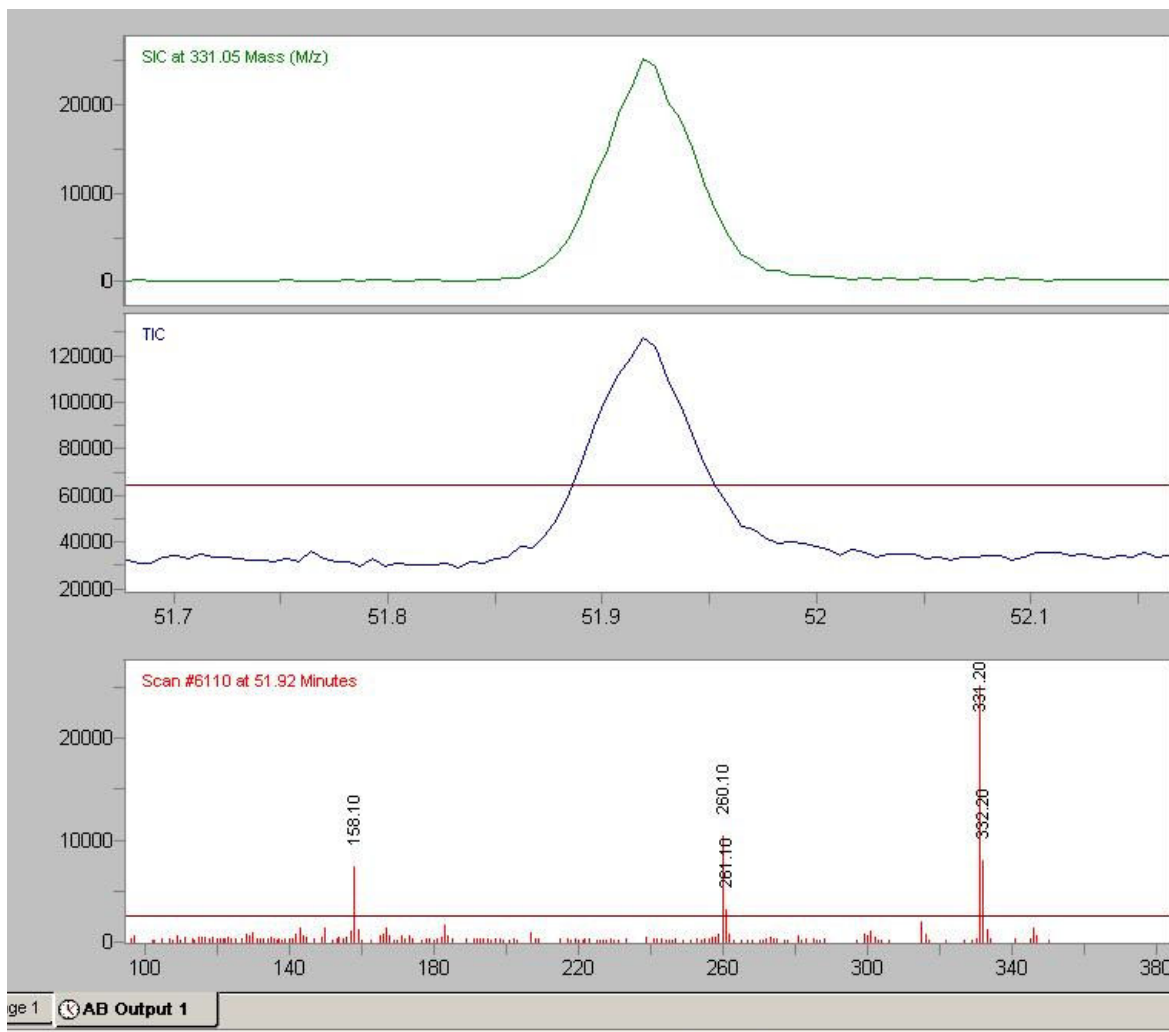


Figure 6: GRAMS spectra for unknown compound 3.

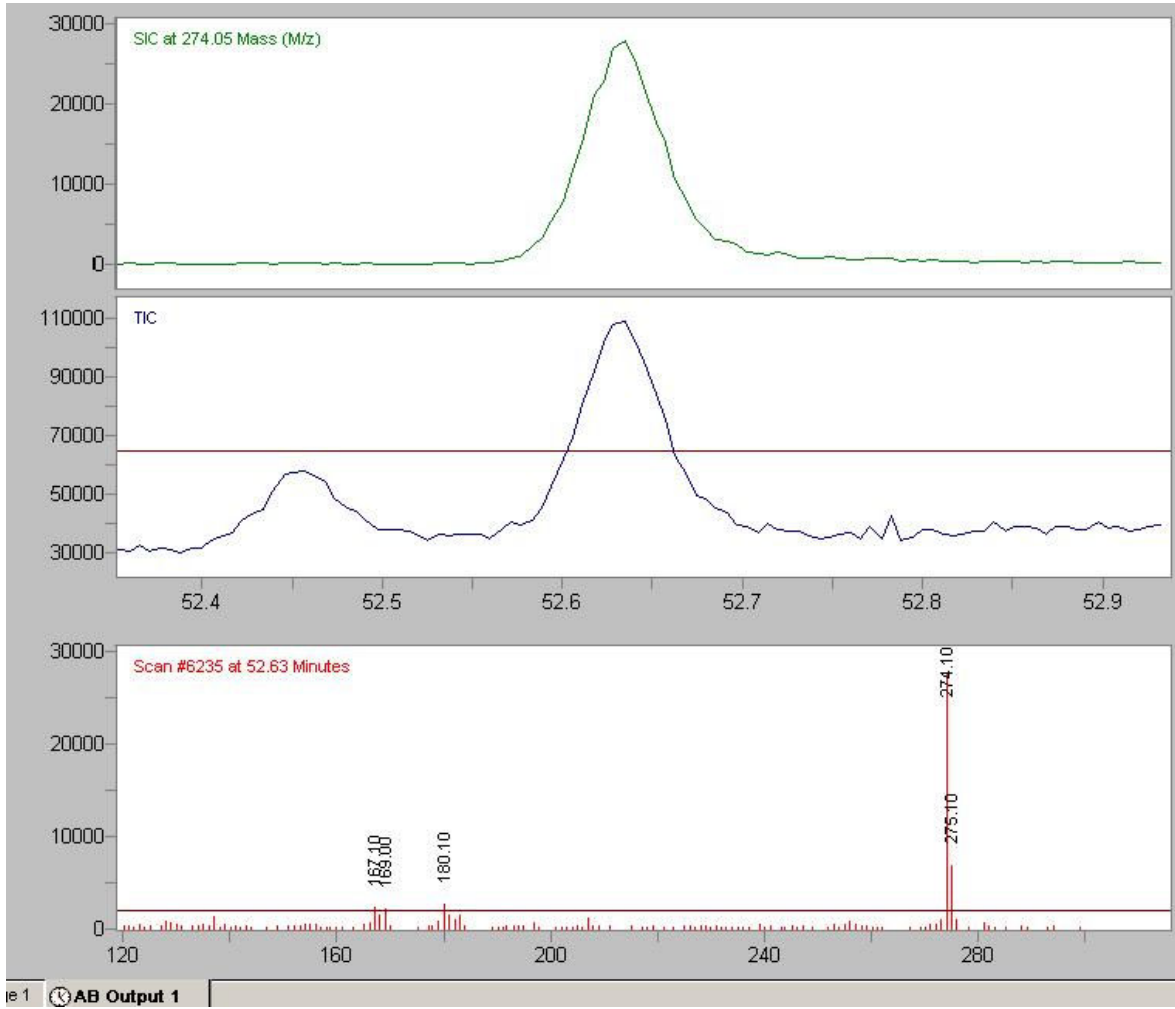


Figure 7: GRAMS spectra for unknown compound 4.

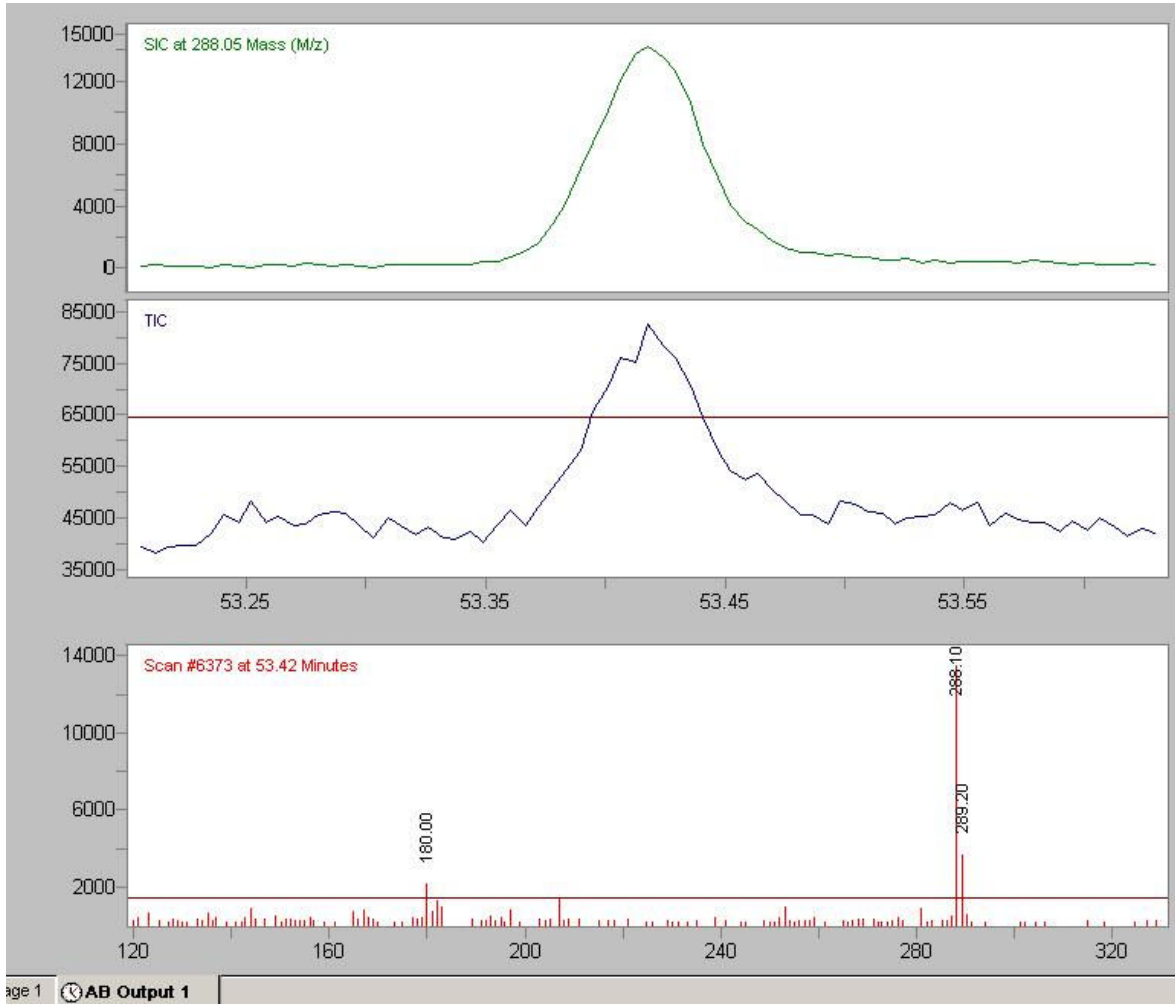


Figure 8: GRAMS spectra for unknown compound 5.



Similar chemical structures were shown as typical components of rubber (Coran, Ohm, 1997). According to the spectra and pattern of fragmentation these compounds can belong to benzothiazoles and benzothiazolesulfenamides widely used as accelerators for sulfur vulcanization. The same compounds have been found in aerosol samples collected in the Deck Park tunnel (see Table 7, B and C).

**Table 7: Concentrations of Potential Tracer Compounds in Tire Tread Samples and in Aerosol Samples from First and Second Deck Park Experiments**

**A. Light Duty and Heavy Duty Tire Wear Composites**

Name	Diagnostic Ion	Light Duty Composite (ppm)	Heavy Duty Composite (ppm)
Compound #3	331	91.51	168.32
Compound #4	274	145.65	202.91

**B. Aerosol Samples. Deck Park Tunnel Experiment I**

Name	Entry S2 (ng/m3)	Vent S2 (ng/m3)
Compound #3	0.188	0.544
Compound #4	0.641	0.871

“Entry” and “Vent” are used for the tunnel inflow and outflow samples. S2 and AF correspond particle size cuts 1.0-10.0 and less than 1.0  $\mu\text{m}$  respectively.

### C. Aerosol Samples. Deck Park Tunnel Experiment II

#### First day of Experiment II

<b>Entry S2</b>	<b>Conc. (ng/m<sup>3</sup>)</b>	<b>Vent S2</b>	<b>Conc. (ng/m<sup>3</sup>)</b>
Compound #3	0	Compound #3	0.168
Compound #4	0.0245	Compound #4	0.293
<b>Entry AF</b>		<b>Vent AF</b>	
Compound #3	0	Compound #3	0
Compound #4	0	Compound #4	0

#### Second day of Experiment II

<b>Non-Vent S2</b>	<b>Conc. (ng/m<sup>3</sup>)</b>	<b>Vent S2</b>	<b>Conc. (ng/m<sup>3</sup>)</b>
Compound #3	0.00319	Compound #3	0.187
Compound #4	0	Compound #4	0.167
<b>Non-Vent AF</b>		<b>Vent AF</b>	
Compound #3	0	Compound #3	0
Compound #4	0	Compound #4	0

Compounds # 3 and # 4 have been identified in the ambient aerosol samples collected in Greater Los Angeles during the SCOS experiment (Allen et al., 2000). Compound # 3 has been also identified in aerosol samples collected in the Caldecott tunnel (California). Compound # 5 has not been identified in these samples.

### 4.2.2 Tire Wear Emission Rate

Using the measured concentrations of tire wear markers, tire wear emission rates per kg of carbon burned in the fuel were determined as:

$$E_i = (C_{i1} - C_{i0}) / (C_{c1} - C_{c0})$$

where  $E_i$  is the emission rate for species  $i$ ;  $C_{i0}$  and  $C_{i1}$  are the concentrations of species  $i$  at the inlet and outlet, respectively.  $C_{c0}$  and  $C_{c1}$  are the concentrations of carbon at the inlet and outlet, respectively. We have successfully used this method to determine emission rates in the Caldecott tunnel (Allen et al., 2001). Since more than 95% of carbon in fuel is converted to  $CO_2$ , concentrations of  $CO_2$  are good approximations of  $C_{c0}$  and  $C_{c1}$ .

Emission rates,  $E_i$ , are based on the amount of fuel burned are stable and very useful for tailpipe emissions, but one expects tire wear emissions to scale with the distance driven. The relative emissions of tire wear for the different paving surfaces will be determined by the change in  $E_i$  between the experiments assuming a constant average fuel economy before and after paving.

### 4.2.3 Tire Wear Emission Rates Based on Tire Wear Tracers

Emission rates measured in the Deck Park tunnel are shown in Tables 8 and 9.

**Table 8: Emission Rates of Tire Wear Tracers Measured in the Deck Park Tunnel (ug/kgC)**

Tire wear tracer	Deck Park tunnel, Experiment 1 (before repaving)	Deck Park tunnel, Experiment 2 (after repaving)
Compound # 3	0.046	0.023
Compound # 4	0.030	0.021

**Table 9: Emission Rates of Tire Wear Tracers Measured in the Deck Park Tunnel (ug/km)**

Tire wear tracer	Deck Park tunnel, Experiment 1 (before repaving)	Deck Park tunnel, Experiment 2 (after repaving)
Compound # 3	0.0038	0.0019
Compound # 4	0.0025	0.0017

Emission rates of both tracer compounds were found higher at PCC road surface layer than at AR-ACFC road surface. This finding confirms the hypothesis that AR-ACFC road surface layer results in less tire wear than PCC road surface layer.

Knowing the concentrations of tire wear tracer compounds in composite samples of tread from used tires in Arizona, we can calculate tire wear emission rates at PCC and AR-ACFC road surfaces as shown in Table 10:

**Table10: Tire Wear Emission Rates Measured in the Deck Park Tunnel (ug/km)**

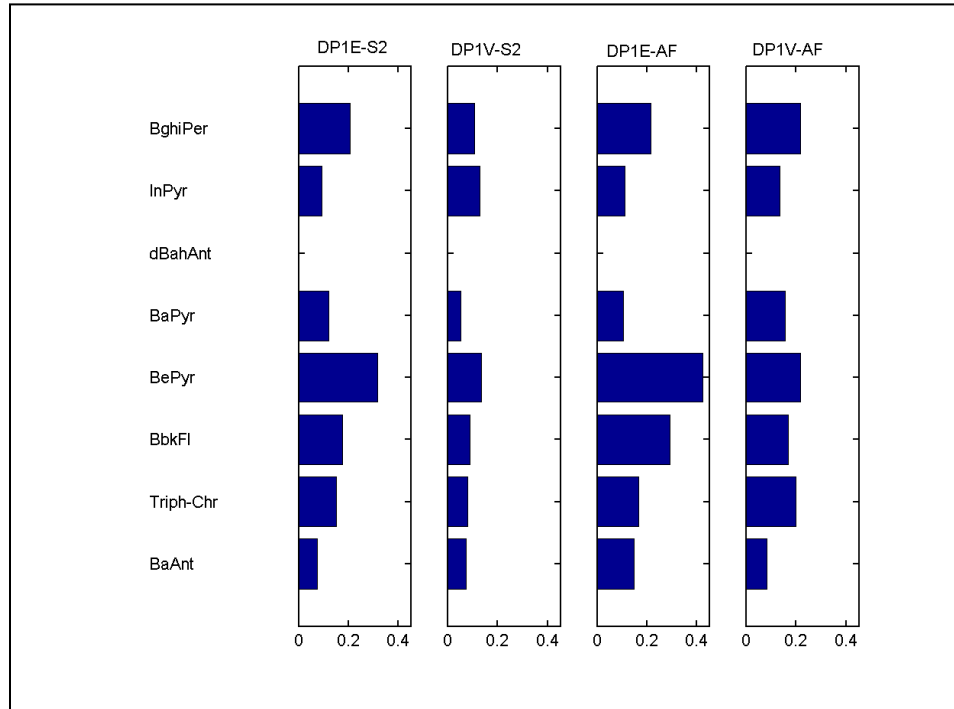
Tire wear emission rate based on	Deck Park tunnel, Experiment 1 (PCC road surface)	Deck Park tunnel, Experiment 2 (AR-ACFC road surface)
Compound # 3	354	177
Compound # 4	172	120

Emission rates of the compound # 3 have been also calculated for two bores of the Caldecott tunnel (California): for mixed fleet of light and heavy duty vehicles 13.52  $\mu\text{g}/\text{kgC}$  and for “light duty vehicles only” 36.46  $\mu\text{g}/\text{kgC}$ . The compound # 4 was not identified in the Caldecott tunnel. Note that characteristics of the fleet driving through the Caldecott tunnel differ from those of the Deck Park tunnel.

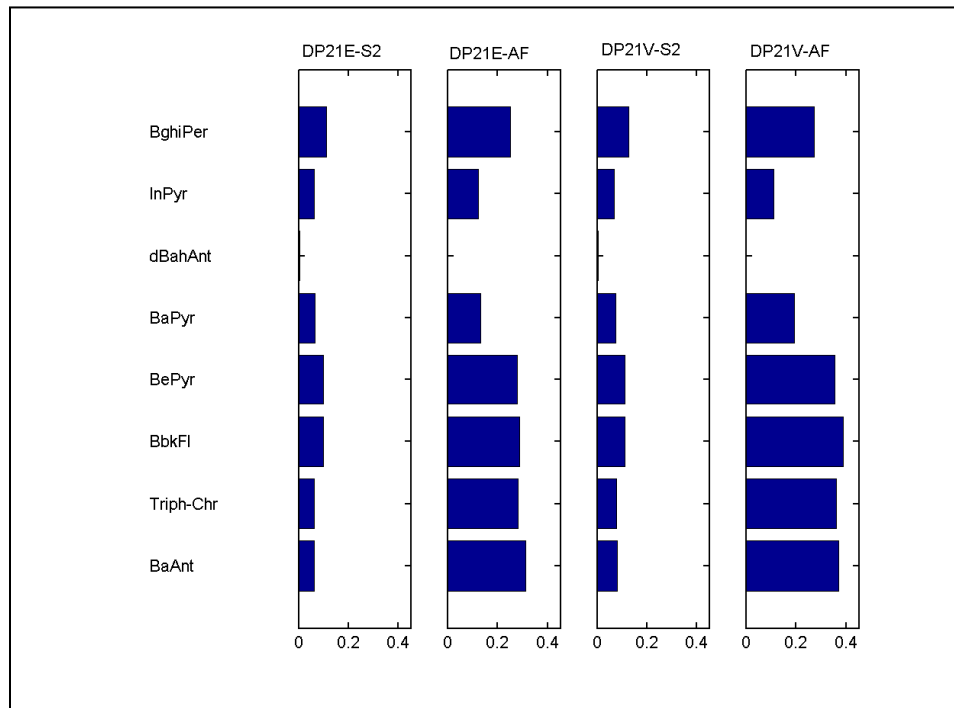
#### 4.2.4 Polycyclic Aromatic Hydrocarbons in the Deck Park tunnel

Polycyclic aromatic hydrocarbons (PAHs) are well known byproducts of combustion (Rogge, 1993; Schauer, 1996). Their chemical features make them easier to identify and quantify than tire wear tracer compounds. Thus, PAH concentrations obtained for the tunnel inflow and outflow samples can be useful to check the quality of measurements, i.e. whether inflow concentrations can be considered as background measurements. The concentrations of 8 aromatic hydrocarbons with a molecular weight from 228 to 278 have been measured.

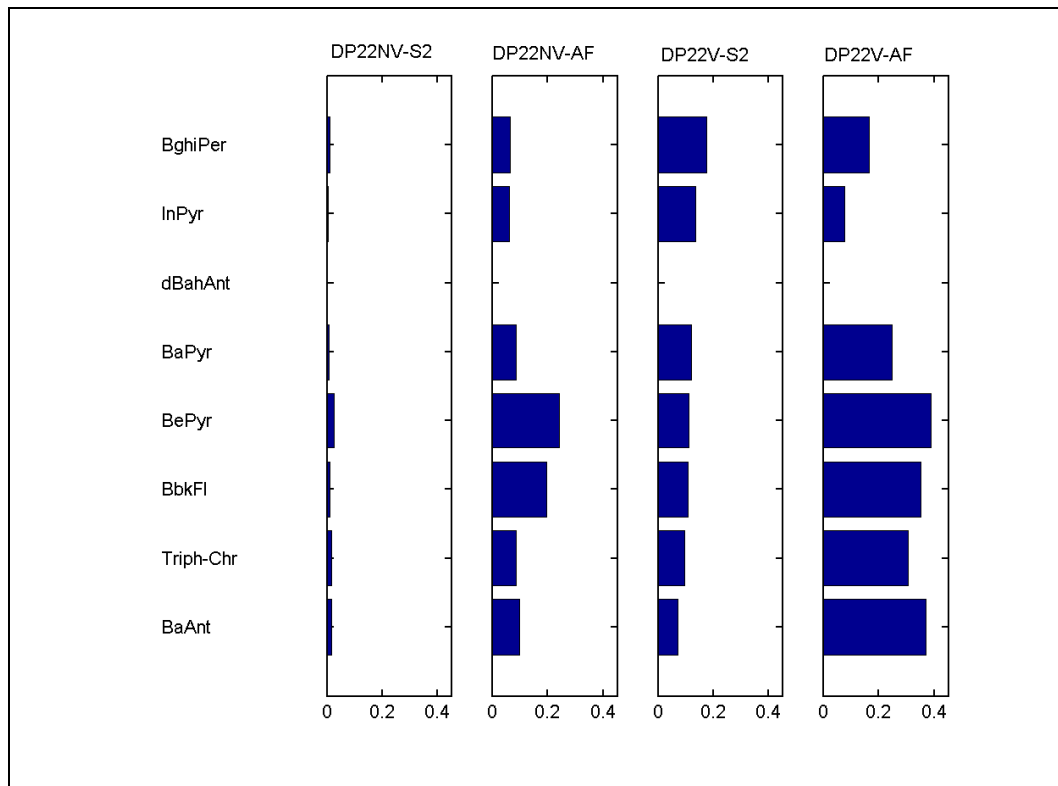
Figures 9 through 11 show PAH concentrations calculated for two Deck Park tunnel experiments. Sample names are organized in the following way: first two letters indicate the site name, i.e. DP corresponds to Deck Park, following numbers 1 and 2 correspond to first and second experiments respectively, letters E and V mean “Entry” and “Vent” respectively, and S2 and AF correspond to particle size cuts 1.0-10.0 and less than 1.0  $\mu\text{m}$  respectively. “Entry” and “Vent” are used for the tunnel inflow and outflow samples.



**Figure 9: PAH concentrations (ng/m<sup>3</sup>) measured in the First Deck Park tunnel experiment (before repaving).**



**Figure 10: PAH concentrations (ng/m<sup>3</sup>) measured during the first day of the Second Deck Park tunnel experiment (after repaving).**



**Figure 11: PAH concentrations (ng/m<sup>3</sup>) measured during the second day of the Second Deck Park tunnel experiment (after repaving).**

PAH concentrations were found lower at Vent than at Entry (both S2 and AF) in the first tunnel experiment. The sampler was positioned on the entrance of westbound (bus platform), which is located between two traffic bounds. The sampler was positioned near the wall separating the two tunnel bounds from another. This wall had a considerable height; and in this case the background was likely affected by particles transported with the air flow over the wall separating sampling site from bore of opposite direction.

PAH concentrations measured during the first day of second tunnel experiment were higher at Vent than at Entry (both S2 and AF), although within 20 % (error limits). Assuming that the background sample may be contaminated inside the tunnel, during the second day of the second tunnel experiment background sample was taken not inside the tunnel but in the Deck Park. The sampler was positioned on the ground approximately two meters from the trailer roof where outflow measurements were taken. For this sample the name “Entry” is changed to NonVent. PAH concentrations were found approximately 3-4 times higher at Vent than at NonVent, particularly at the Stage 2. PAH concentrations are approximately twice higher at afterfilter than at Stage 2. It was reported that high molecular weight PAHs (molecular weight > 252) are preferentially associated with a fraction  $D_a < 1.0 \mu\text{m}$  (Allen et al., 2001).

PAH profiles from Vent are different at Stage 2 and afterfilter: Stage 2 shows higher concentrations of high molecular PAHs with MW > 252 while PAHs with MW < 252 dominate at afterfilter sample. PAH profile at Stage 2 is more similar to that one reported for light duty gasoline-powered vehicles. PAH profile at afterfilter is more similar to that one reported for heavy duty diesel-powered vehicles (Rogge et al., 1993).

PAH concentrations in the Deck Park tunnel are lower but comparable to those measured in the Caldecott tunnel (mixed fleet). The profiles (Caldecott PM1.9, mixed fleet and Stage 2 Deck Park) are similar.

Study of PAH concentrations in the inflow and outflow samples showed that measurements made during the first Deck Park tunnel experiment and the first day of the second Deck Park tunnel experiment provided overestimated values of background concentrations. This fact obviously affects the correctness of measurements made during the first Deck Park experiment. Although we still can conclude that emission rates of tire wear tracer compounds were higher on the PCC road surface layer than on AR-ACFC road surface because if the background values were actually lower, in this case emission rates of organic tracers measured in the outflow samples during the first tunnel experiment (before repaving) can be even higher than calculated and showed in the Tables.

### **4.3 Roadway Characteristics**

The roughness and frictional characteristics of a pavement surface play an important role in road safety and tire wear. Factors such as tire geometry, traveling speed of the vehicle, the minuscule surface structure between the interfacing contact areas (texture), and contamination of the pavement surface play an important role on the frictional characteristics of the pavement.

To better understand the interaction of the tire and pavement surface in this experiment, roughness measurements (IRI), and frictional characteristics (macro-texture) were measured by ADOT.

#### **4.3.1 Roughness Measurements**

One important characteristic that gives an indication of the pavement functional condition is the roughness. Pavement roughness is the distortion of the road surface that contribute to an undesirable and uncomfortable ride. ADOT utilizes a profilometer to measure the International Roughness Index( IRI). IRI is the ratio of the accumulated suspension motion to the distance traveled expressed in units of inches per mile. The index summarizes the longitudinal surface profile in a wheelpath.

The IRI provides a numeric scale of measuring roughness; this scale range from 0 to 1267 in/mi with larger values indicating greater roughness. The approximate break point between what is considered rough and smooth pavement is often considered to be 125

in/mi. The specific FHWA guidelines that relates IRI levels to condition is presented in Table 11.

**Table 11: Relation between IRI and condition (FHWA 1999)**

Condition categories	IRI rating (in/mi)	
	Interstate	Other
Very good	<60	<60
Good	60-94	60-94
Fair	95-119	95-170
Mediocre	120-170	171-220
Poor	>170	>220

ADOT Pavement Management Division performed the IRI measurement of the east and west bound lanes of the tunnel section, before and after the overlay with the AR-ACFC. Five lanes in each direction east and west were measured; lanes 1-4 plus the HOV lane.

Plots that compare the surface profiles are included in Appendix A. Table 12 below summaries the IRI measurements before and after the overlay. As expected, it is observed that an improvement in the IRI was obtained. All of the IRI values were below 60 in/mi.

**Table 12: IRI measurements before and after the AR-ACFC overlay.**

SECTION	IRI (in/mi)	
	PCCP	AR-ACFC
I010EHOV	96.34	43.57
I010ELN1	123.20	59.03
I010ELN2	104.29	48.81
I010ELN3	111.87	47.80
I010ELN4	115.30	52.91
I010WHOV	85.44	32.51
I010WLN1	87.94	37.79
I010WLN2	85.40	46.92
I010WLN3	96.83	46.11
I010WLN4	97.75	36.81



### 4.3.2 Friction Measurements

Another important characteristic in assessing a pavement functional characteristics is the surface friction. Pavement surface friction is the force developed at the tire-interface that resists sliding when braking forces are applied to the vehicle tires.

ADOT utilizes a MU meter or Side Force testing device. Side force testers are designed to simulate a vehicle's ability to maintain control at curves. They function by maintaining a test wheel in a plane at an angle to the direction of motion, while the wheel is allowed to roll freely. The developed side force is then measured perpendicular to the plane of rotation. Measurements are reported as a skid number, that is, the measured value of friction times 100. In Arizona, the intervention level for friction reported for interstate, primary and secondary roadways is 34 (MuMeter).

ADOT Pavement Management Division performed the surface friction measurements on the east and west bound lanes of the tunnel section, before and after the overlay with AR-ACFC. Similar to the roughness measurements, the five lanes in each direction, east and west bound lanes, were tested; these are lanes 1-4 plus the HOV lane.

The plots to compare the surface friction values for each lane before and after the overlay are included in Appendix B. Table 13 below shows a summary of the values obtained. The data shows an improvement in the skid numbers after the overlay.

**Table13: Friction test data summary.**

SECTION	AVERAGE FRICTION VALUE(MU)	
	PCCP	AC
I010EHOV	0.54	0.66
I010ELN1	0.6	0.61
I010ELN2	0.49	0.61
I010ELN3	0.47	0.6
I010ELN4	0.47	0.54
I010WHOV	0.51	0.58
I010WLN1	0.64	0.57 *
I010WLN2	0.5	0.59
I010WLN3	0.44	0.59
I010WLN4	0.42	0.58

Note:

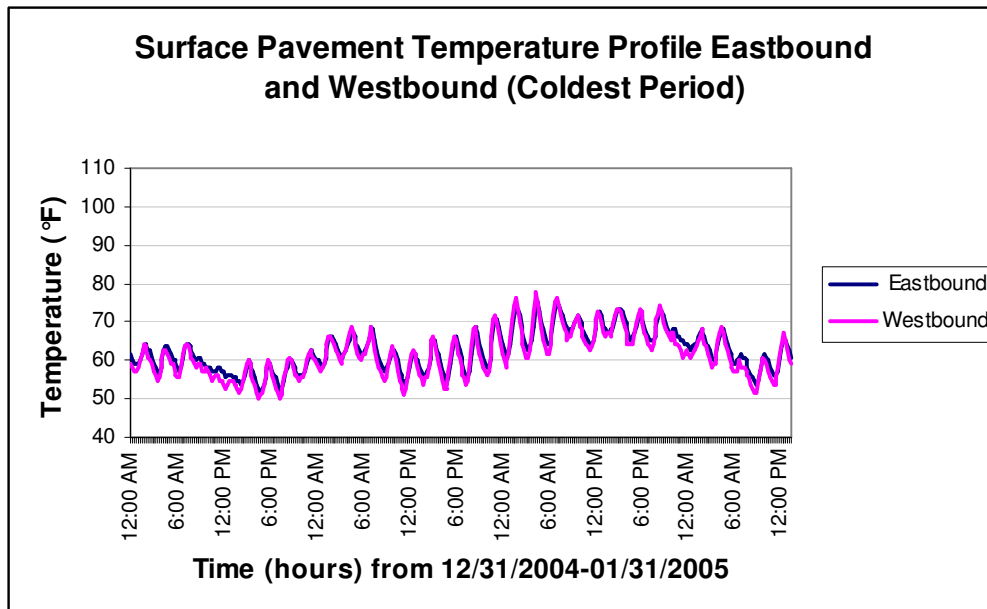
\* Average value lower after overlay

### 4.3.3 Pavement Temperature

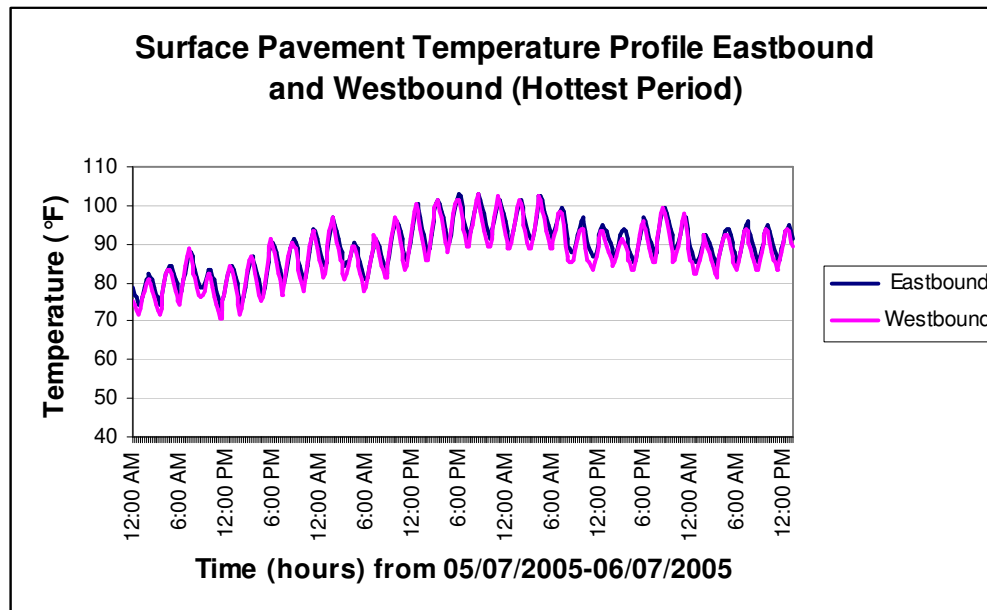
Temperature thermistors (COMMAND Center Button Sensors) were also installed to monitor the pavement surface temperatures inside and outside the tunnel. Unfortunately, the sensors outside the tunnel were damaged by the compaction process during the overlay of the AR-ACFC. Sensors inside the tunnel were functioning (access to retrieve the data was a challenge since there are no parking shoulders inside the tunnel).

Data of pavement surface temperature were collected for the east and westbound lanes inside the tunnel. For the eastbound tunnel, temperature data were collected every 20 minutes from October 17<sup>th</sup> to November 14<sup>th</sup> 2004. For the westbound tunnel, pavement surface temperatures were collected from October 24<sup>th</sup> to November 21<sup>st</sup> 2004.

Figures 12 and 13 below shows typical pavement temperature profile for the east and westbound tunnels; Figure 12 reflects a period of cool weather conditions (December 31<sup>st</sup> 2004 to January 31<sup>st</sup> 2005); whereas, Figure 13 reflects a period of warmer weather conditions (May 7<sup>th</sup> to June 6<sup>th</sup> 2005). The data shows that the eastbound lanes had slightly higher pavement temperatures compared to the westbound lanes.



**Figure 12: Surface Pavement Temperature Profile, December – January.**



**Figure13: Surface Pavement Temperature Profile, May – June.**

## 5 Conclusions

1. Tire wear tracer compounds have been identified and quantified in representative tire wear composite samples from used tires in Arizona, ambient aerosol samples and aerosol samples collected from two roadway tunnels. Test extraction and separation protocols to determine the amounts of tire wear tracers in tire treads have been developed.
2. Emission rates of tire wear tracer compounds have been calculated. Emission rates of tire wear tracers were found higher at PCC road surface than at AR-ACFC road surface. This finding supports the hypothesis that AR-ACFC road surface layer results in significantly less tire wear than PCC road surface layer.
3. Emission rates of tire wear per kilometer driven have been calculated. Emission rates of tire wear per kilometer driven at PCC road surface are 1.4-2 times higher than emission rates of tire wear at AR-ACFC road surface. These findings provide ADOT with tire wear emission data for use in the federally-mandated air quality modeling for the Phoenix airshed.
4. Roughness and frictional characteristics of the pavement surface after the AR-ACFC overlay have been improved as shown by the IRI and skid numbers measurements, respectively.

## 6 Acknowledgements

Thanks are due to Arnold Burnham, ADOT's Project Manager of this research effort, Arnold Burnham, Kathleen Sommer and Mark Wheaton, who were the contact and organizers of the project schedule, James Delton, Assistant State Engineer, Dennis Rusher and Ernie Johnson, Pavement Management Division; Edward Walsh and John Kruger of the ADOT tunnel maintenance department were extremely helpful in providing logistical support including access to the tunnel, electric power, and a bucket truck. We could not have done this experiment without their kind assistance. Thanks are also due to George Way (ADOT, retired) for his help in the early stage when the idea and project scope was being formulated.

Several ASU graduate students assisted in this study in different capacities. They are: Daniel Gonzales, Maria Carolina Rodezno, and Qinyue Sun.

## 7 References

Allen J. O., Dookeran N. M., Taghizadeh K., Lafleur A. L., Smith K. A., and Sarofim A. F., 1996: Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts, *Environ. Sci. Technol.*, 30:1023-1031.

Allen J. O., Mayo P. R., Hughes L. S., Salmon L. G., Cass G. R.. Emissions of size-segregated aerosols from on-road vehicles in the Caldecott Tunnel, *Environ. Sci. Technol.*, 35:4189-4197, 2001.

Coran A.Y. Vulcanization. In Encyclopedia of Polymer Science and Technology. U. S. Environmental Protection Agency, *MOBILE 6.1 Particulate Emission Factor Model Technical Description*, EPA420-R-03-001, 2003.

Gertler A. W., Sagebiel J. C., Wittorff D. N., Pierson W. R., Dippel W. A., Freeman D., Sheetz L., 1997: Vehicle Emissions in Five Urban Tunnels, Final Report to Coordinating Research Council, Project E-5.

Hildemann L.M., Mazurek, M.A., Cass G.R., Simoneit B.R.T., 1991: Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.*, 25:1311-1325.

Kumata H., Takada H., Ogura N., 1996: Determination of 2-(4-morpholinyl) benzothiazole in environmental samples by a gas chromatograph equipped with a flame photometric detector, *Anal. Chem.*, 68:1976-1981.

Kumata H., Sanada Y., Takada H., and Ueno T., 2000: Historical trends of N-cyclohexyl-2-benzothiazolamine, 2-(4-morpholinyl)benzothiazole, and other anthropogenic contaminants in the urban reservoir sediment core, *Environ. Sci. Technol.*, 34:246-253.

Kumata H., Yamada J., Masuda K., Takada H., Sato Y., Sakurai T., and Fujiwara K., 2002: Benzothiazolamines as tire-derived molecular markers: Sorptive behavior in street runoff and application to source apportioning, *Environ. Sci. Technol.*, 36:702-708.

Ohm R.F. Rubber Chemicals. In Kirk-Othmer Encyclopedia of Chemical Technology. 1997.

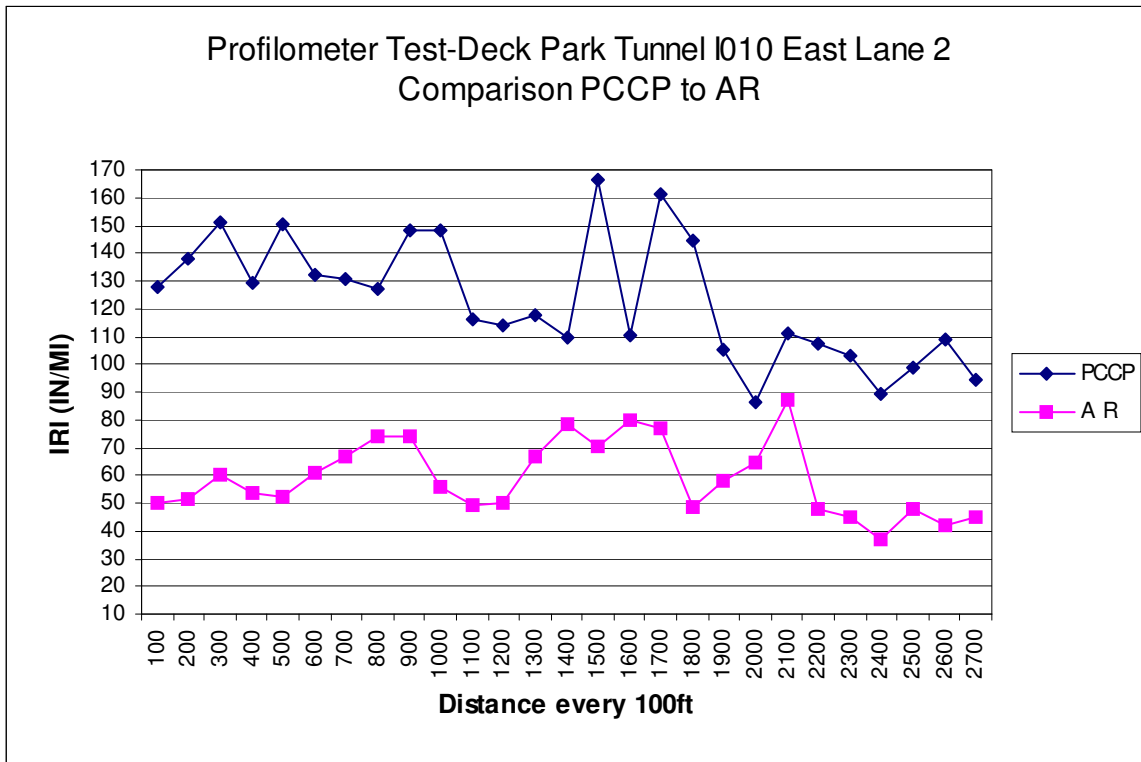
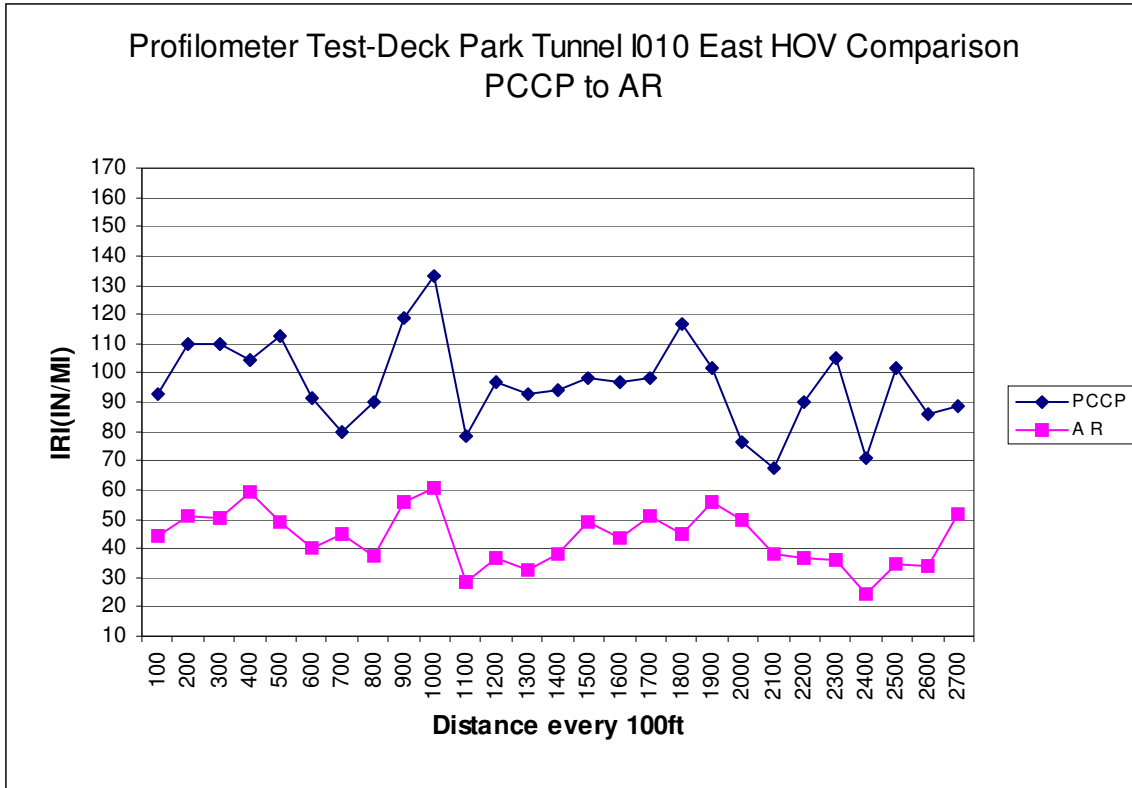
Reddy C. M., Quinn J. G., 1997: Environmental Chemistry of Benzothiozols Derived from Rubber, *Environ. Sci. Technol.*, 31:2847-2853.

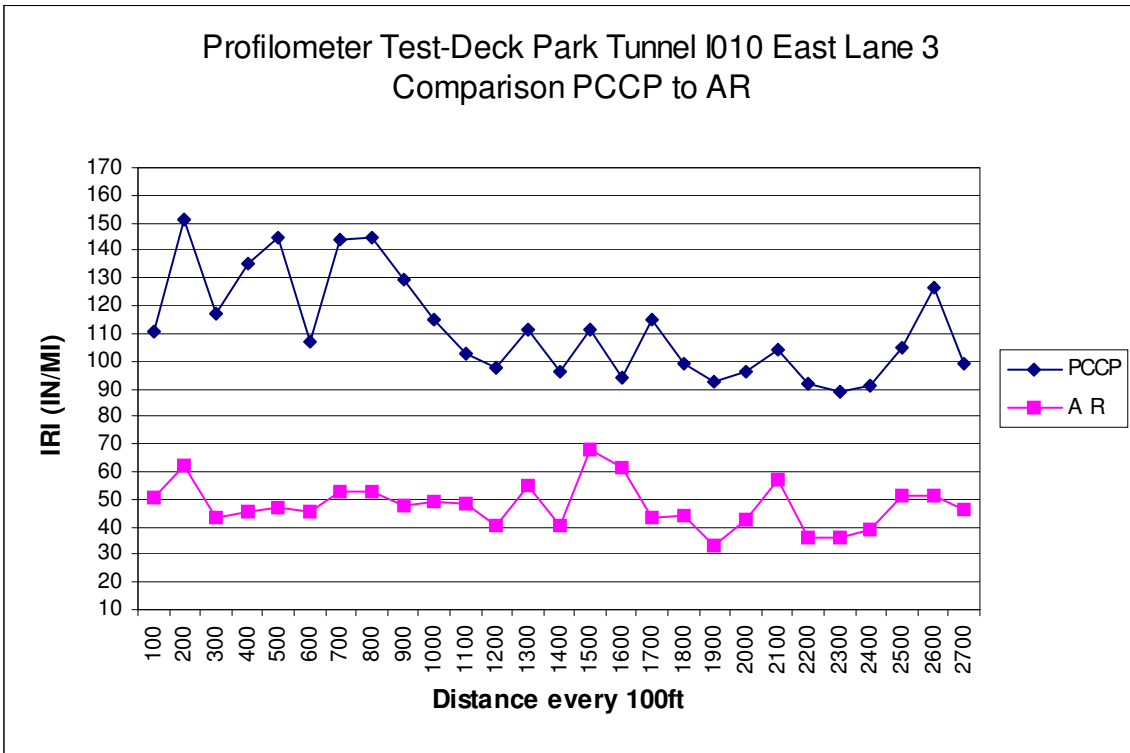
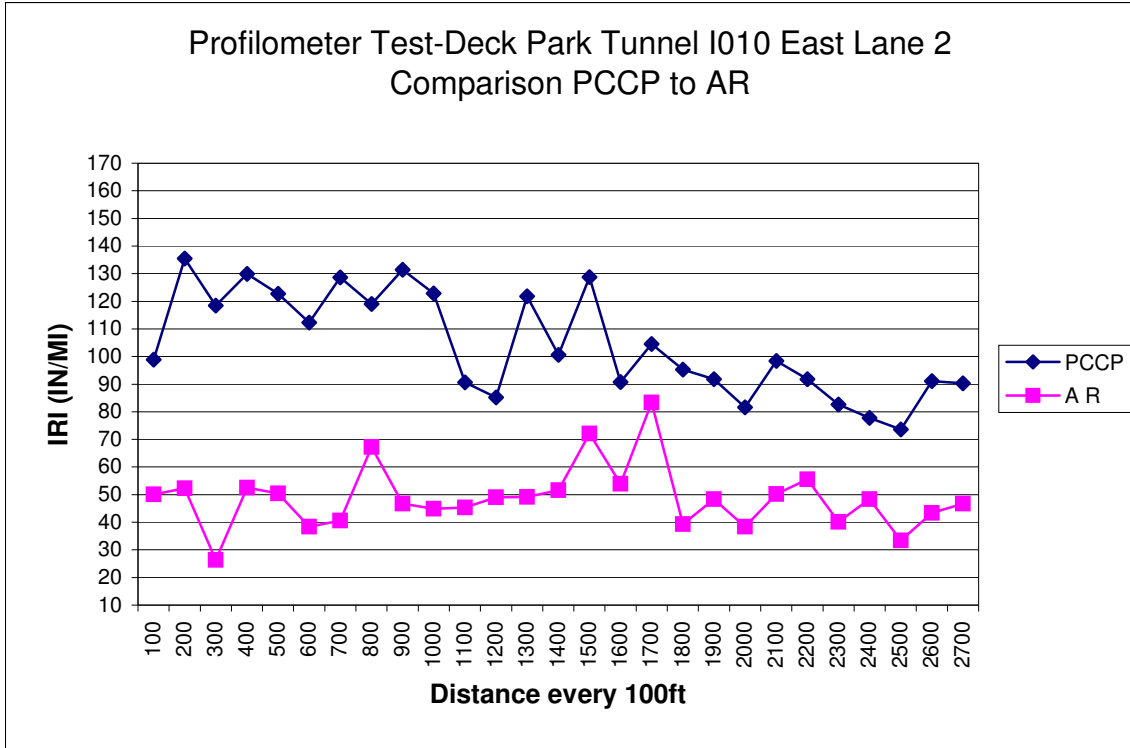
Rogge, W.F., Hildemann L.M., Mazurek, M. A., Cass, G. R., Simoneit, B. R. T., 1993: Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, *Environ. Sci. Technol.*, 27:636-651.

Schauer, J.J., Rogge, W. F., Hildemann, L.M., Mazurek, M. A., Cass, G. R., Simoneit, B. R. T., 1996: Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.*, 30, 3837-3855.

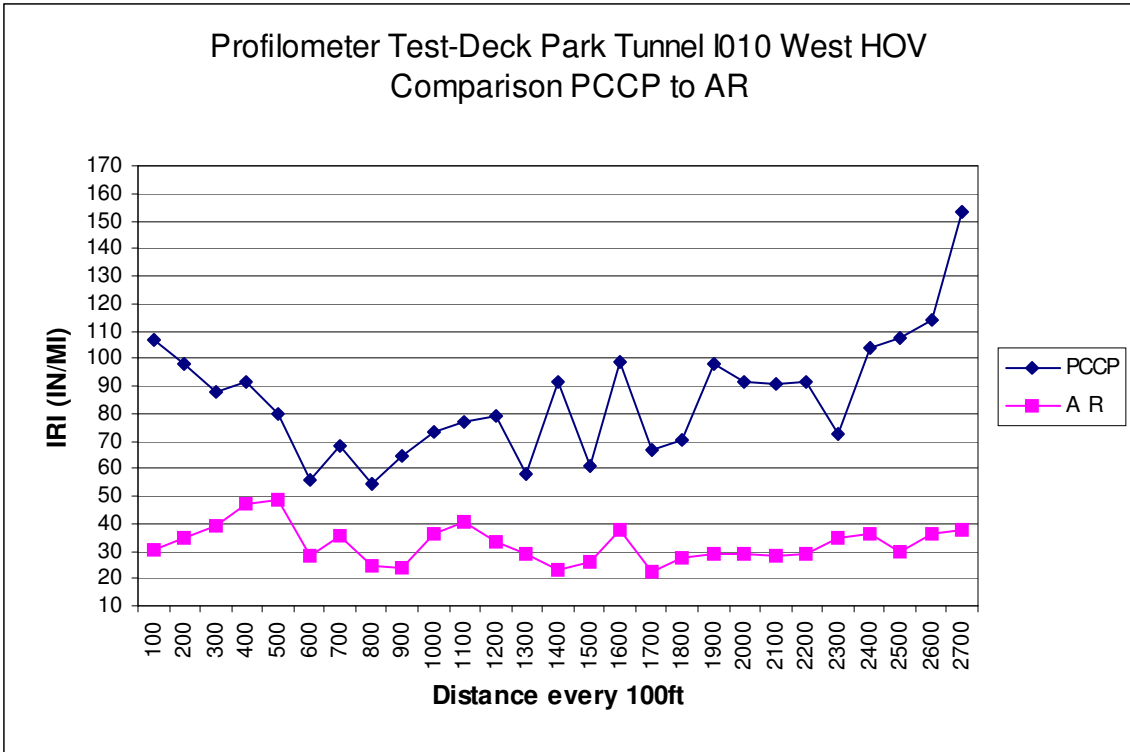
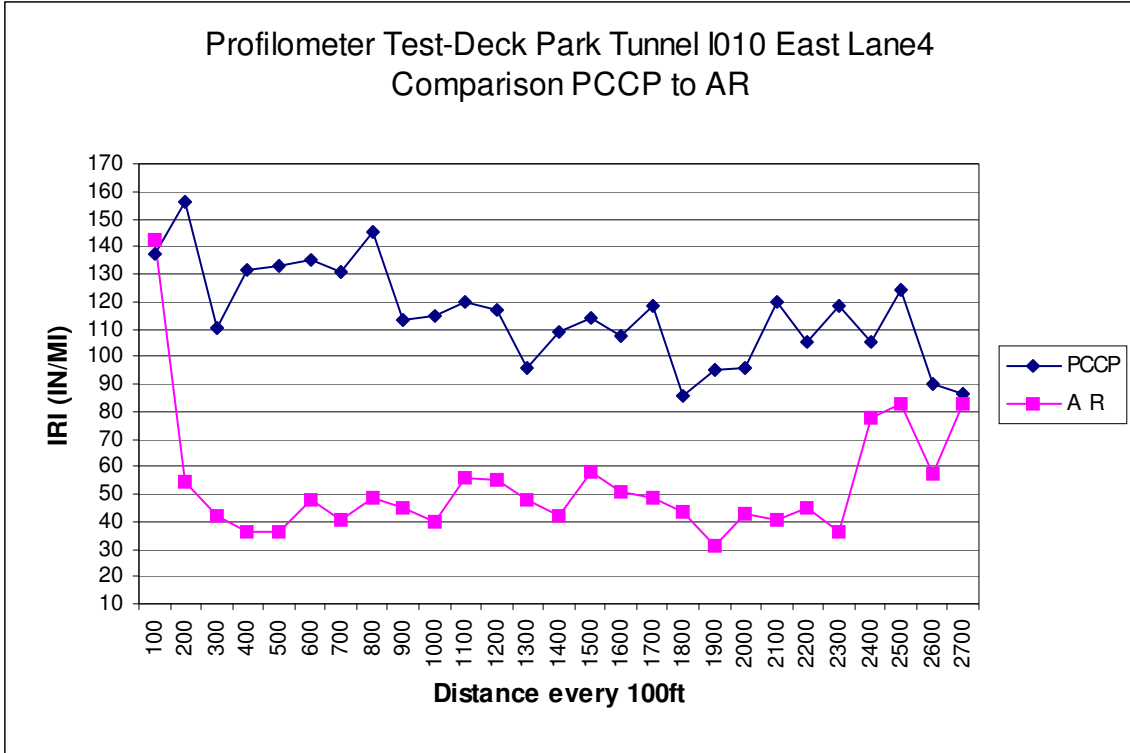
Schauer J.J., Kleeman M.J., Glen G.R., and Simoneit B.R.T., 1999: Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks, *Environ. Sci. Technol.*, 33:1578-1587.

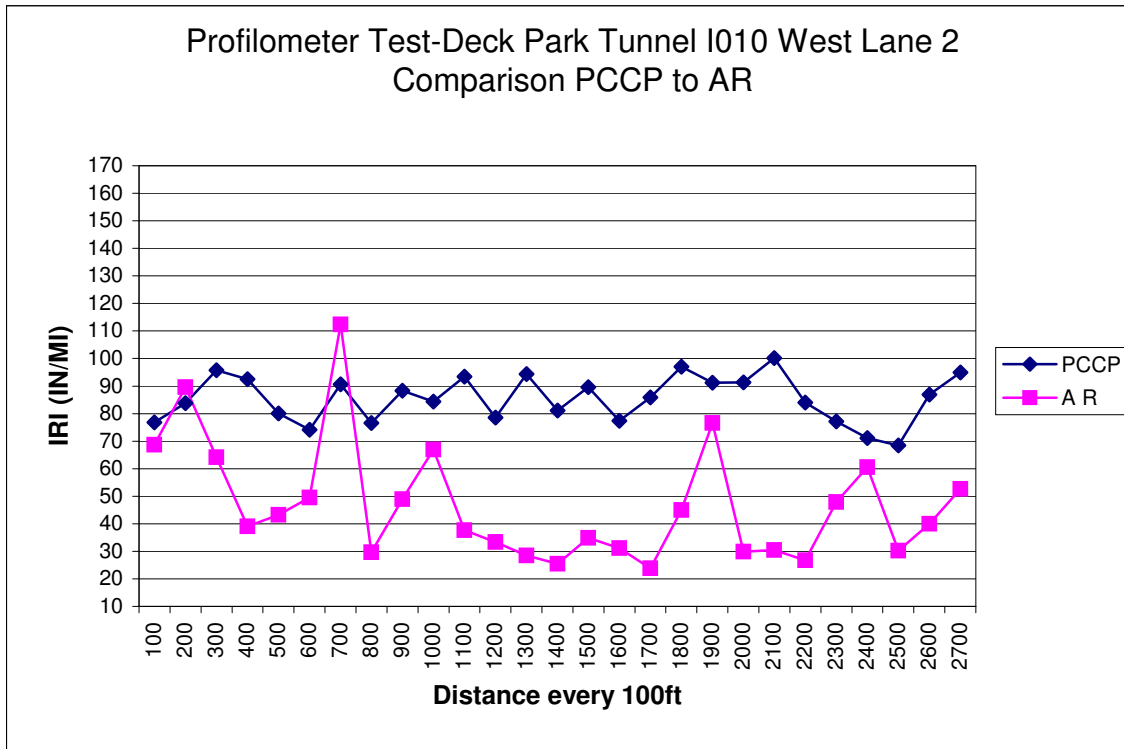
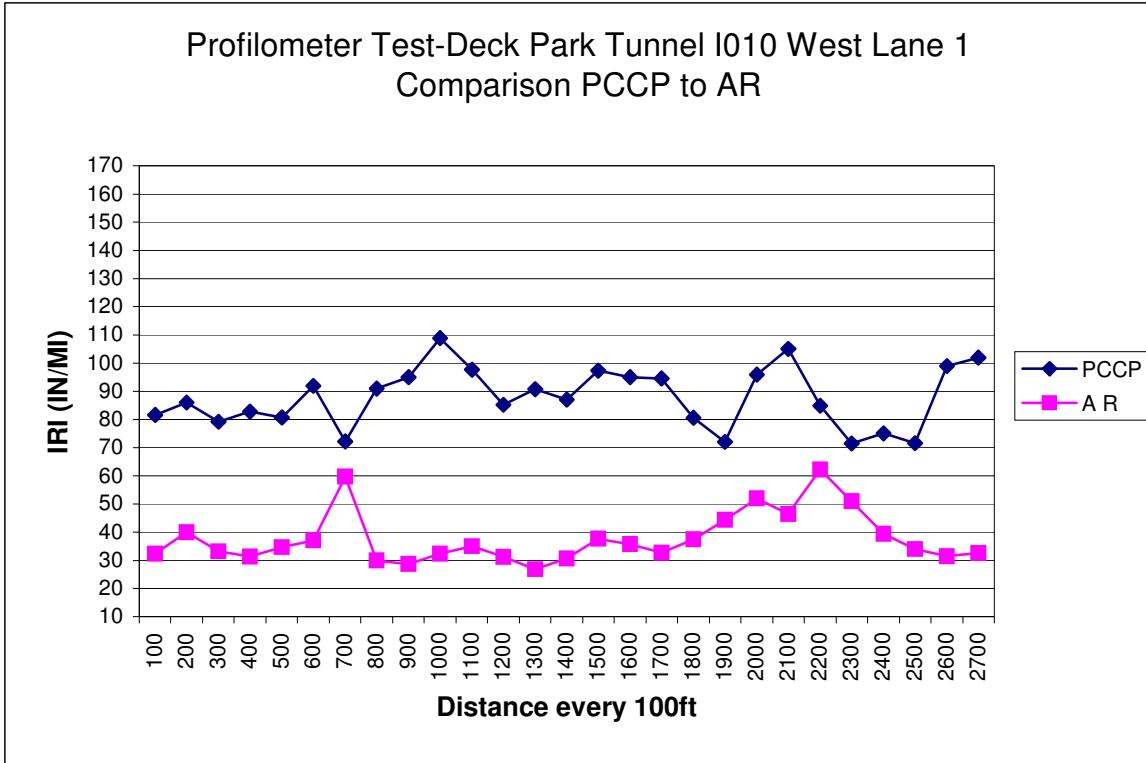
APPENDIX A:  
IRI TEST RESULTS

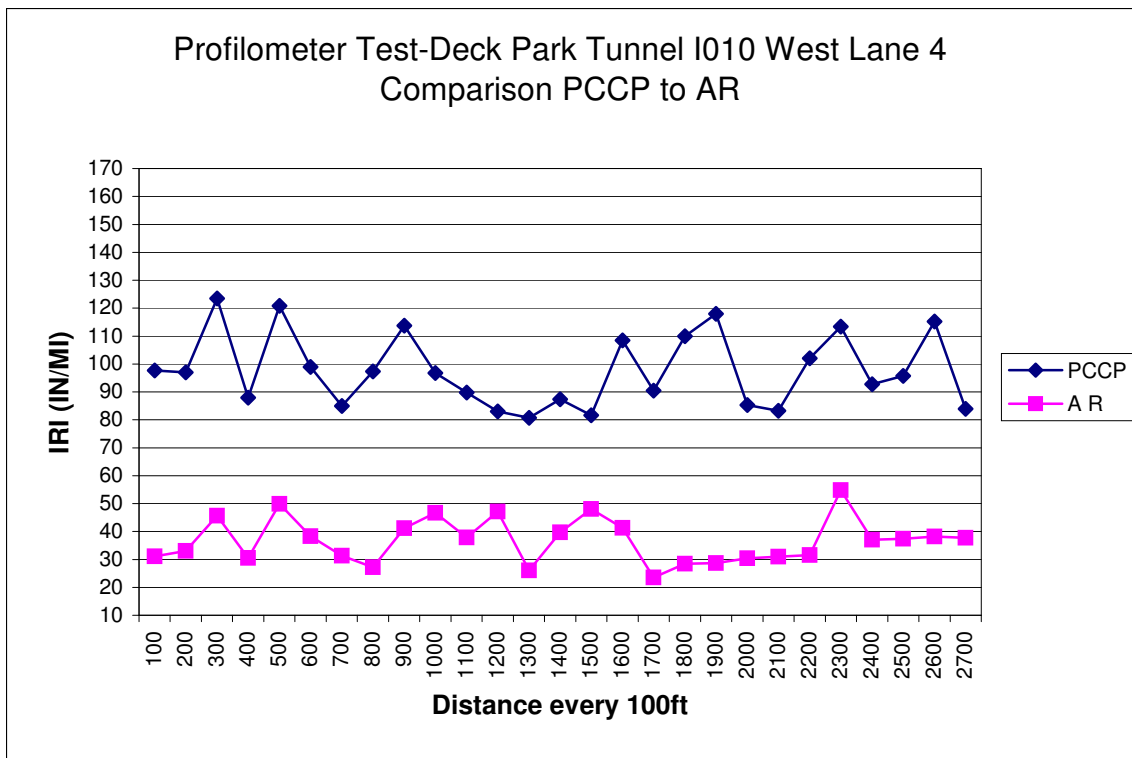
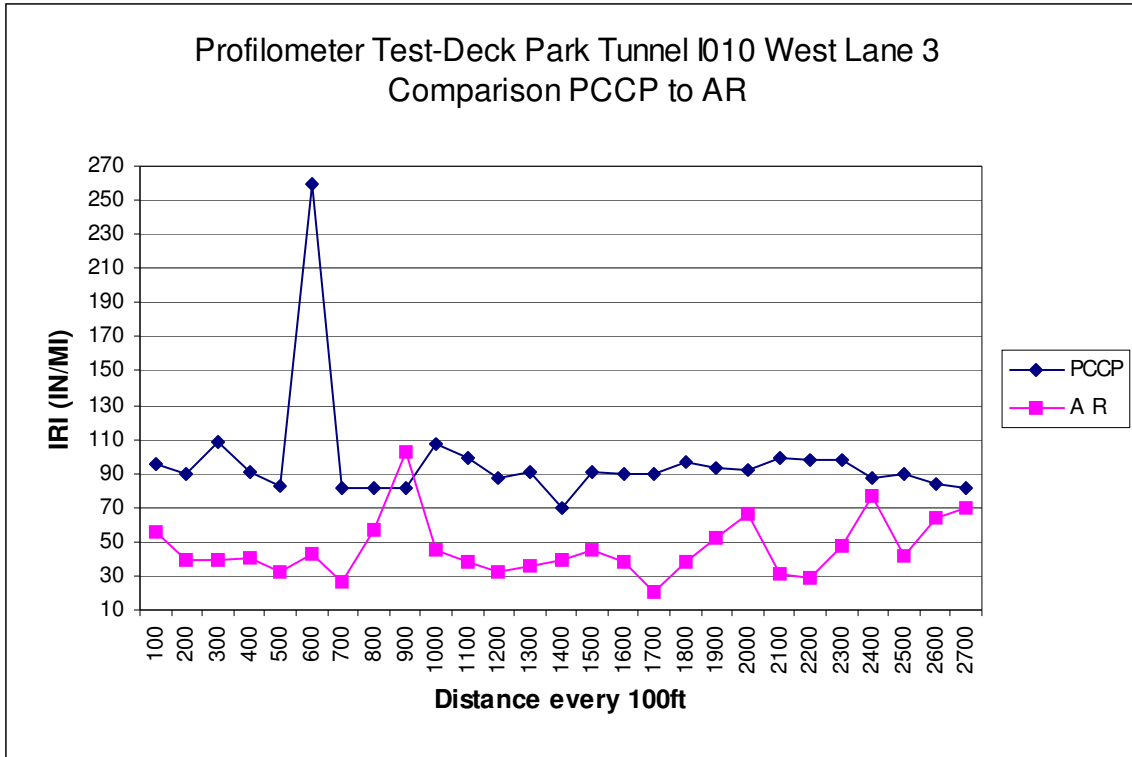






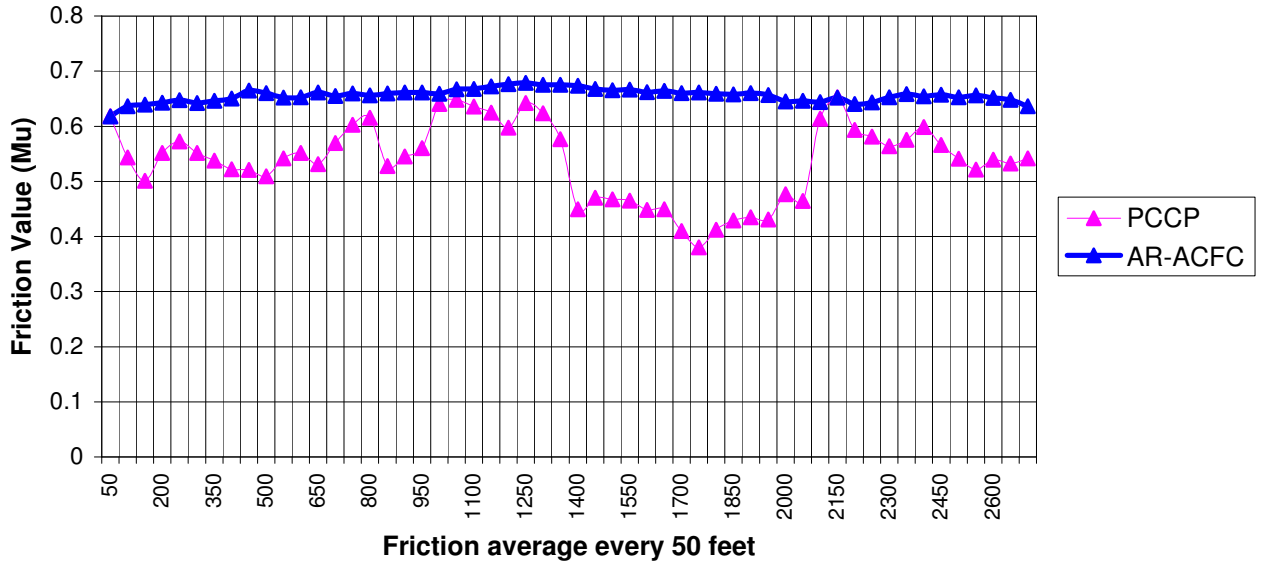




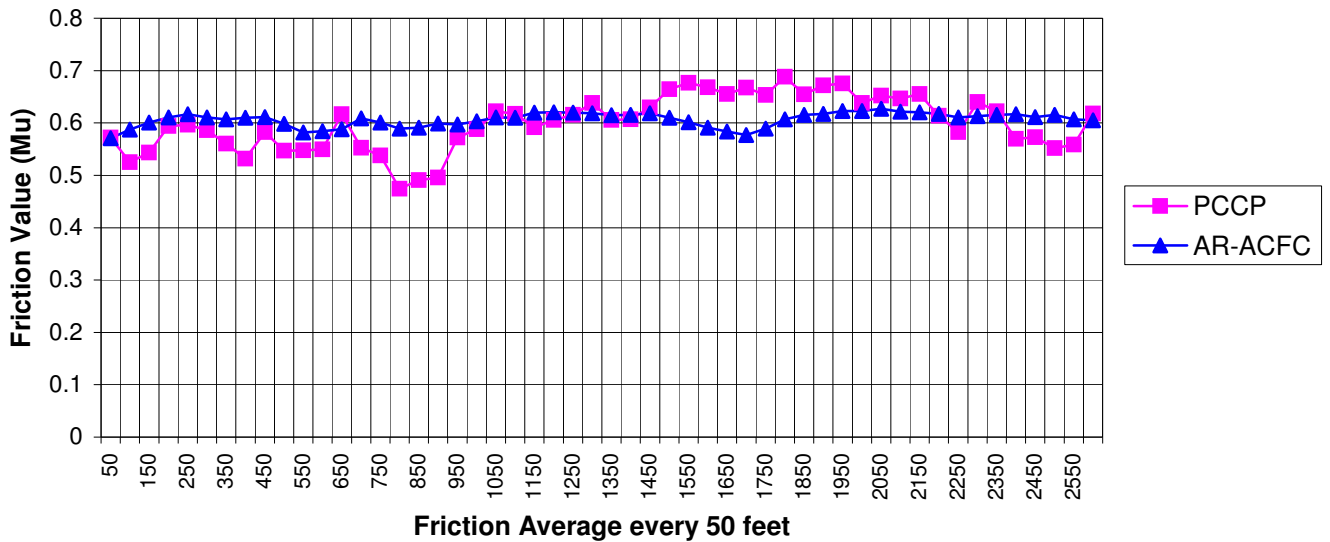


APENDIX B.  
FRICTION TEST RESULTS

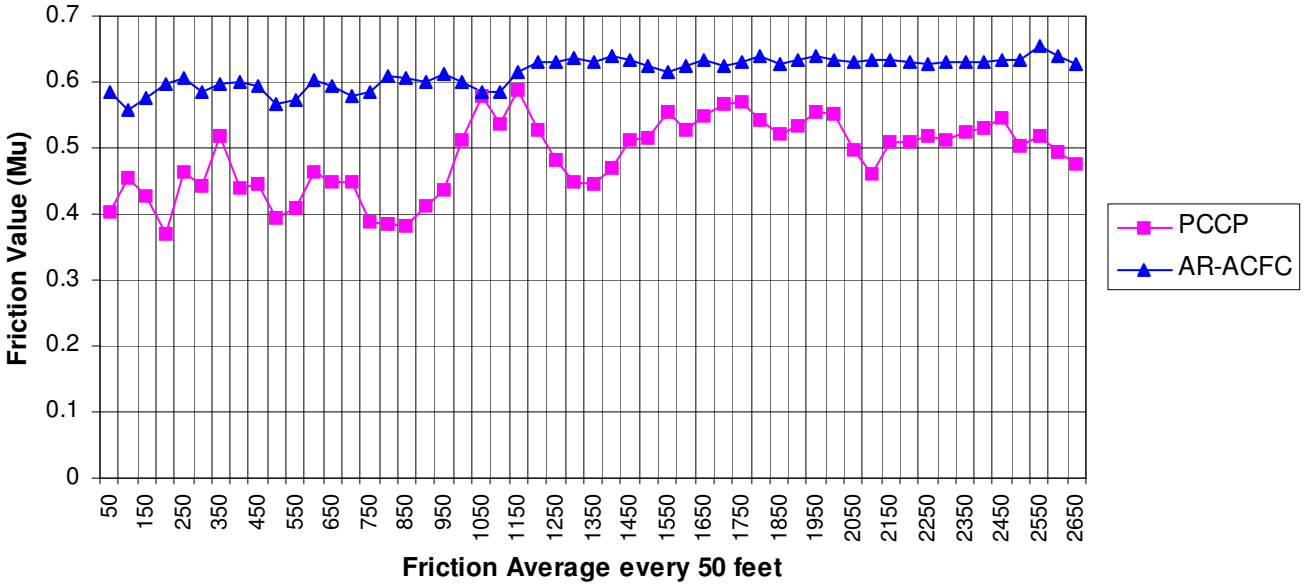
### Friction Test-Deck Park Tunnel I010 East HOV Lane @ 60 mph Comparison PCCP to AR-ACFC



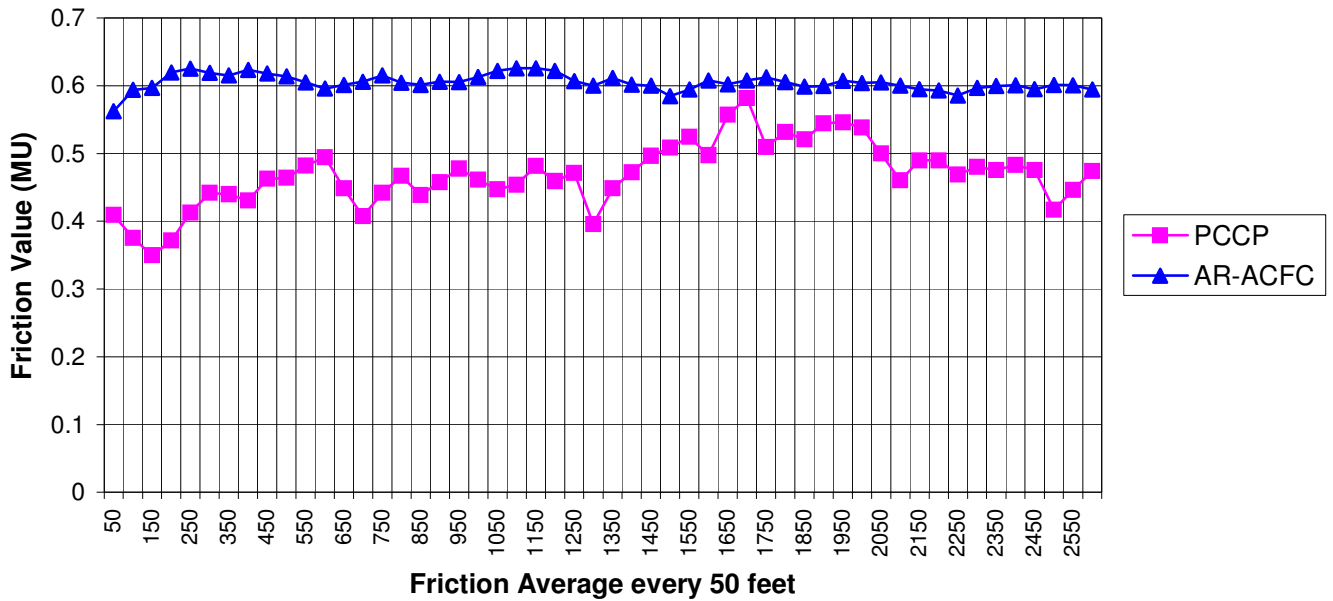
### Friction Test-Deck Park Tunnel I010 East Lane 1 @ 60 mph Comparison PCCP to AR-ACFC



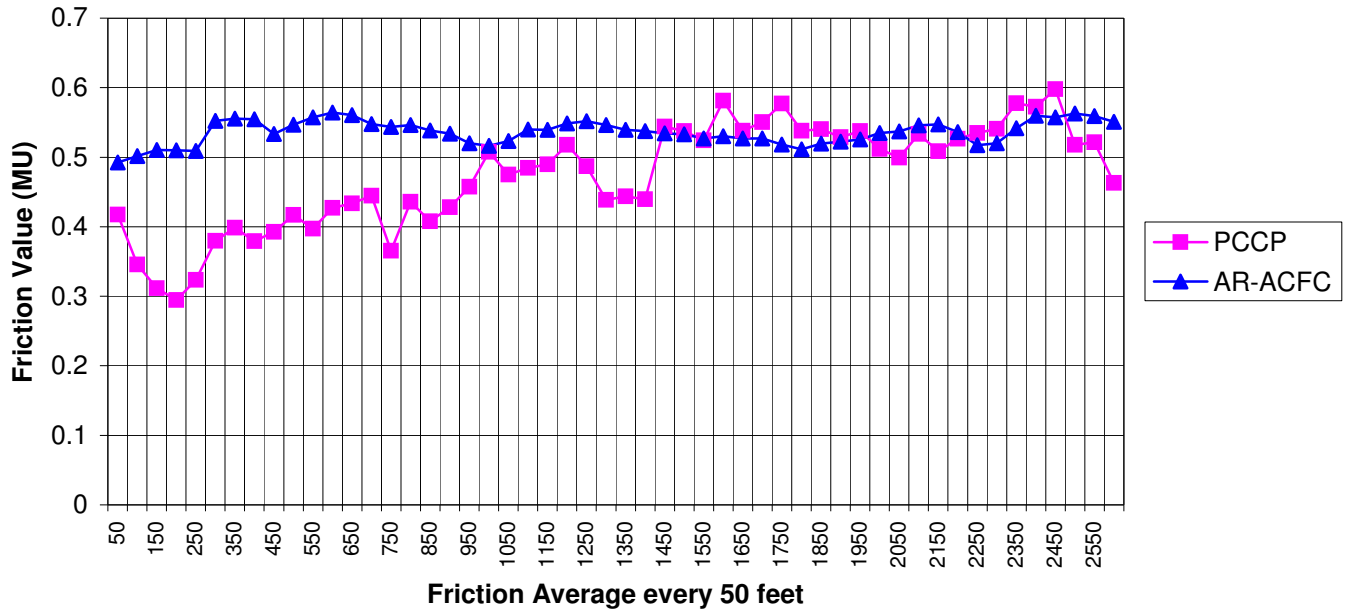
### Friction Test-Deck Park Tunnel I010 East Lane 2 60 mph Comparison PCCP to AR-ACFC



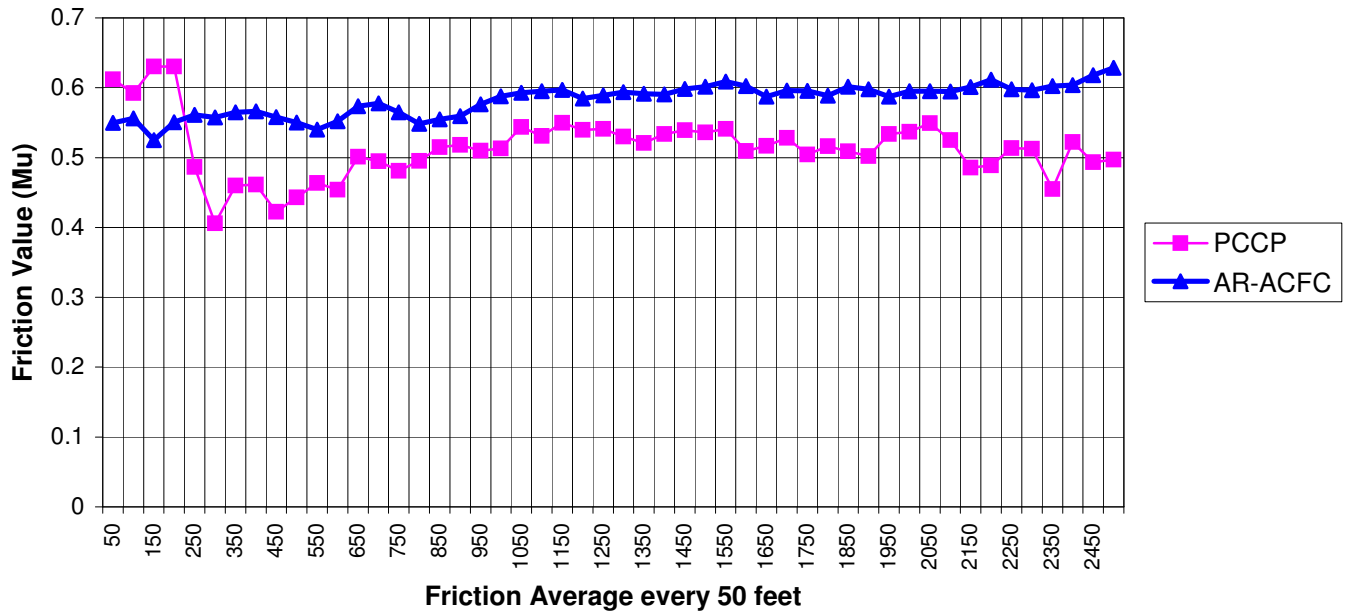
### Friction Test-Deck Park Tunnel I010 East Lane 3 @ 60 mph Comparison PCCP to AR-ACFC



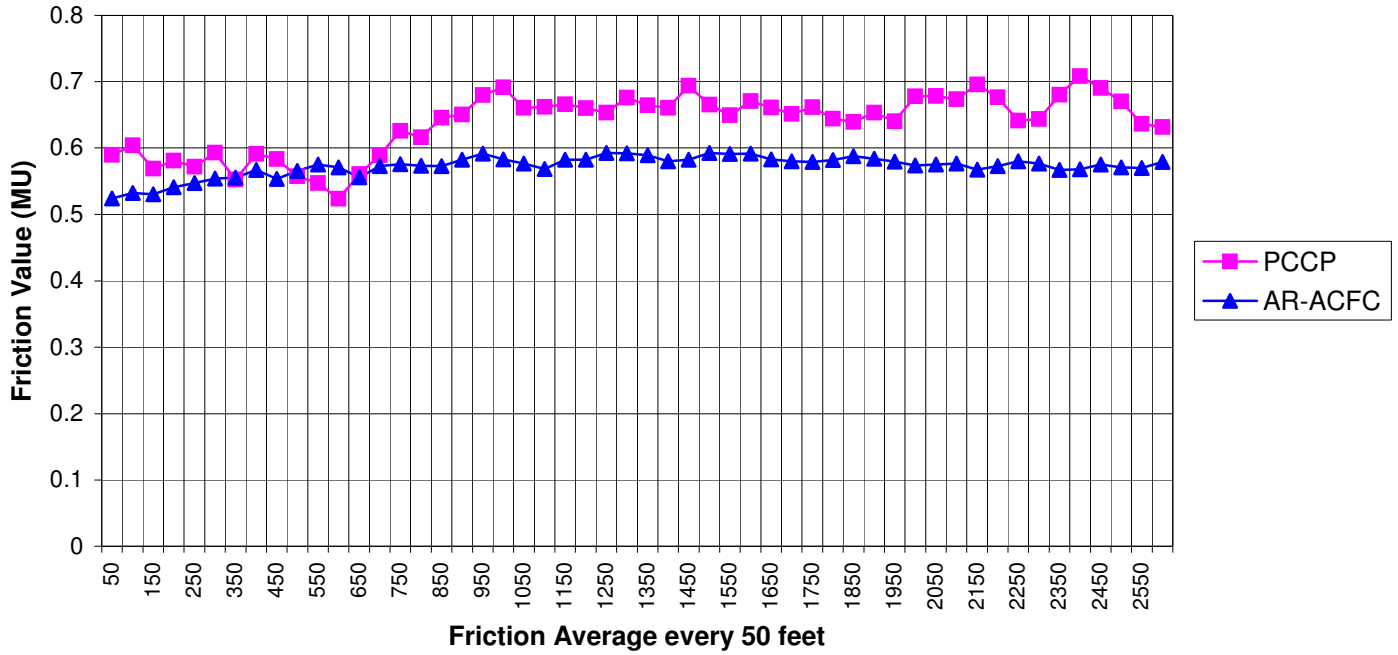
### Friction Test-Deck Park Tunnel I010 East Lane 4 @ 60 mph Comparison PCCP to AR-ACFC



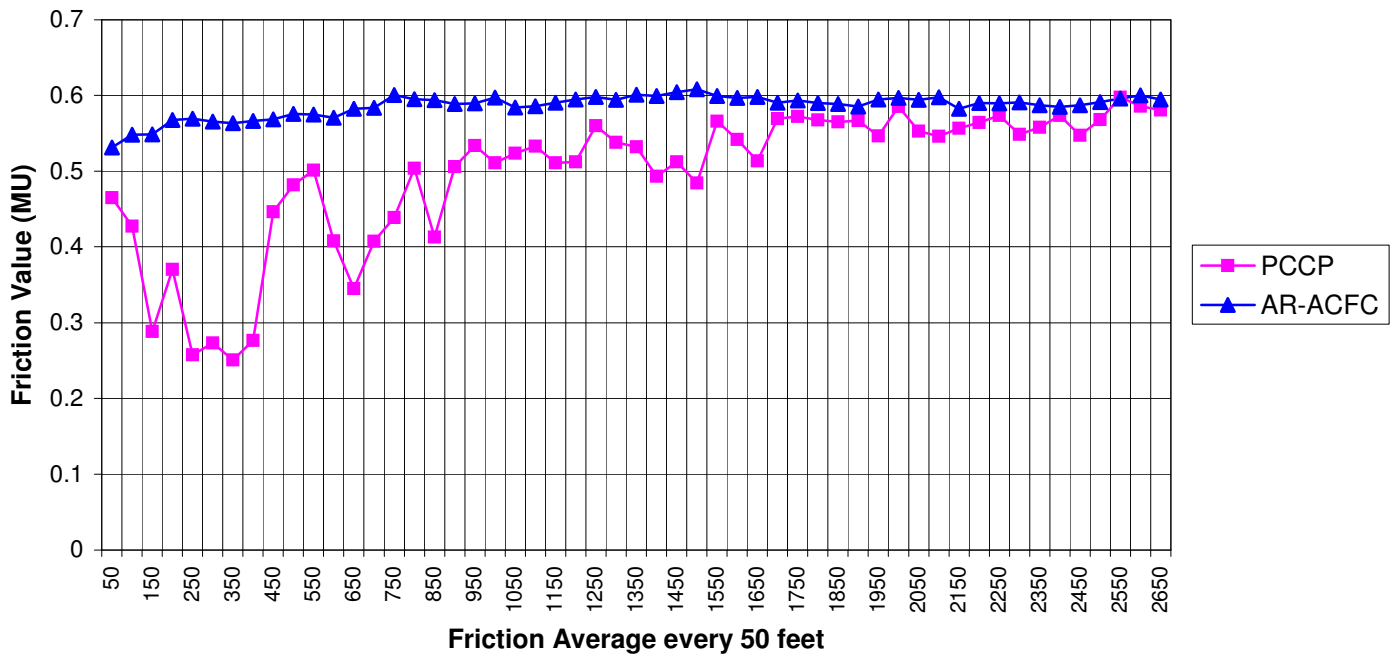
### Friction Test-Deck Park Tunnel I010 West HOV Lane @ 60 mph Comparison PCCP to AR-ACFC



### Friction Test-Deck Park Tunnel I010 West Lane 1 @ 60 mph Comparison PCCP to AR-ACFC

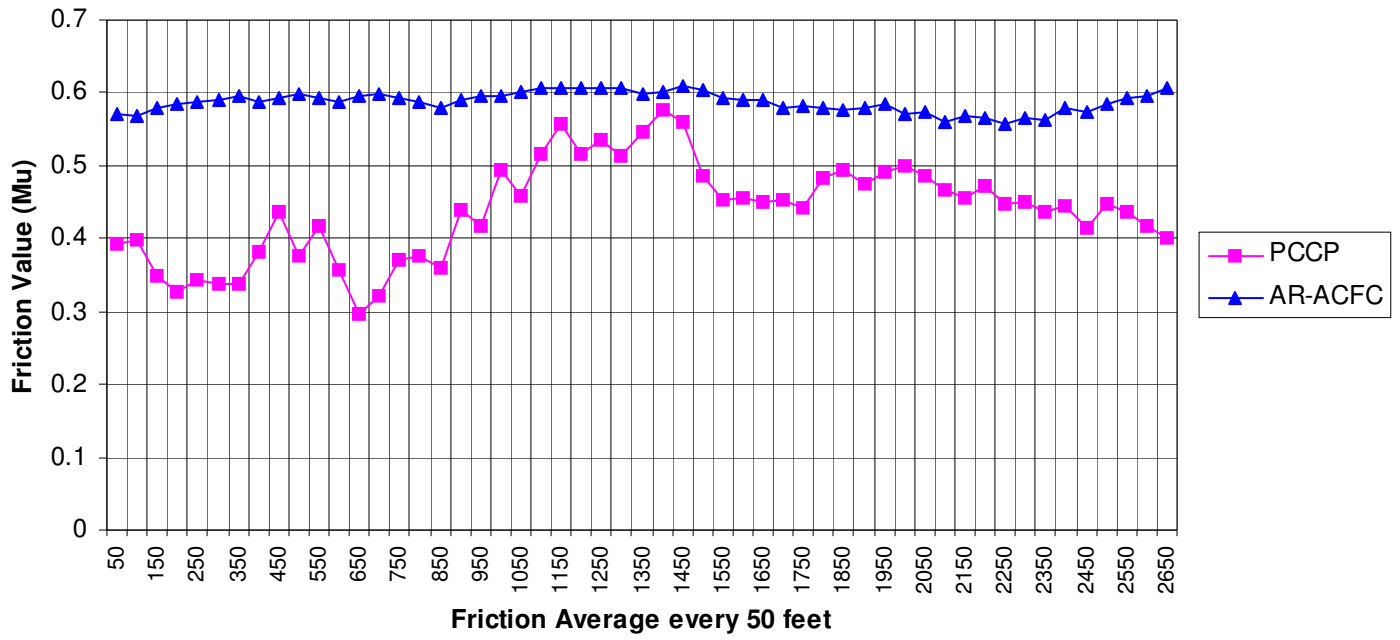


### Friction Test-Deck Park Tunnel I010 West Lane 2 @ 60 mph Comparison PCCP to AR-ACFC





### Friction Test-Deck Park Tunnel I010 West Lane 3 @ 60 mph Comparison PCCP to AR-ACFC



### Friction Test-Deck Park Tunnel I010 West Lane 4 @ 60 mph Comparison PCCP to AR-ACFC

