

# A Fuel-Based Approach to Estimating Motor Vehicle Cold-Start Emissions

**Brett C. Singer, Thomas W. Kirchstetter, and Robert A. Harley**

*Department of Civil and Environmental Engineering, University of California, Berkeley, California*

**Gary R. Kendall and James M. Hesson**

*Technical Services Division, Bay Area Air Quality Management District, San Francisco, California*

## ABSTRACT

The temporary ineffectiveness of motor vehicle emission controls at startup causes emission rates to be much higher for a short period after starting than during fully warmed, or stabilized, vehicle operation. Official motor vehicle emission inventories estimate that excess emissions during cold-start operation contribute a significant fraction of all hydrocarbon, carbon monoxide (CO), and nitrogen oxide (NO<sub>x</sub>) emissions from California vehicles. In an effort to verify these estimates under real-world conditions, vehicle emissions were measured in an underground parking garage in Oakland, CA, during March 1997. Hot stabilized emissions were measured as vehicles arrived at the garage in the morning, and cold-start emissions were measured as vehicles exited in the afternoon; the incremental, or excess, emissions associated with vehicle starting were calculated by difference. Composite emissions from ~135 vehicles were sampled during each of six morning and six afternoon periods. Measured stabilized exhaust emissions were  $19 \pm 2$  g nonmethane hydrocarbons (NMHC),  $223 \pm 17$  g CO, and  $8.6 \pm 1.3$  g NO<sub>x</sub> per gal of gasoline consumed. Cold-start emissions of  $69 \pm 2$  g

NMHC/gal,  $660 \pm 15$  g CO/gal, and  $27.8 \pm 1.2$  g NO<sub>x</sub>/gal were measured for vehicles spending an average of ~60 sec in the garage after starting in the afternoon. Using second-by-second emissions data from California's light-duty vehicle surveillance program, average fuel use during cold start was estimated to be ~0.07 gal, and the cold-start period was estimated to last for ~200 sec. When cold-start emission factors measured in the garage were scaled to represent the full 200-sec cold-start period, incremental start emission factors of 2.1 g NMHC, 16 g CO, and 2.1 g NO<sub>x</sub> per vehicle start were calculated. These emission factors are lower than those used by California's motor vehicle emission inventory model (MVEI 7G) by 45% for NMHC, 65% for CO, and 12% for NO<sub>x</sub>. This suggests that the importance of cold-start emissions may be overstated in current emission inventories. Overall, the composition of volatile organic compound (VOC) emissions measured during cold start was similar to that of hot stabilized VOC emissions. However, the weight fractions of unburned fuel and acetylene were higher during cold start than during hot stabilized driving.

## IMPLICATIONS

Cold starts are thought to contribute a large fraction of total emissions from California's motor vehicle fleet. This study suggests that the importance of cold-start emissions may be overstated, and that control strategies that focus exclusively on reducing cold-start emissions may not achieve projected improvements in air quality. Instead, greater emphasis should be placed on reducing warm running emissions from in-use vehicles. Transit-oriented strategies such as park-and-ride lots may also provide greater air quality benefits than previous assessments have indicated, especially if travel by older, high-emitting vehicles can be reduced.

## INTRODUCTION

Motor vehicle tailpipe emissions of carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), and hydrocarbons (HC) have been reduced substantially since the late 1960s by technological controls that reduce pollutant formation during combustion and remove pollutants from exhaust gases. Strict stoichiometric control of the air-fuel ratio results in lower levels of CO and HC production relative to fuel-rich operation, and lower levels of NO<sub>x</sub> production relative to fuel-lean combustion. Stoichiometric air-fuel mixtures are also required for the treatment of exhaust gases by three-way catalytic converters, which simultaneously oxidize HC and CO to carbon dioxide (CO<sub>2</sub>) and reduce NO to N<sub>2</sub>. New vehicles, equipped with these

and other emission controls, typically emit less than 5% of the pollutants emitted by pre-control vehicles.<sup>1</sup>

One limitation of current vehicle emission control systems is that they are ineffective for a short period after a vehicle is started. At startup, the fuel-air mixture is intentionally enriched to facilitate ignition and improve cold engine operation. This enrichment leads to increased production of CO and HC during combustion, and limits the oxidation of these pollutants in the catalytic converter. In addition, automobile catalysts must reach temperatures above 400–700 °F before significant pollutant conversion is achieved.<sup>2,3</sup> If a vehicle is inactive for more than ~30–60 min before being started, the catalyst will cool significantly. As a result, the catalyst may be ineffective or only partially effective for some additional time after the initial fuel-enrichment period ends. Since the catalytic converter is heated by engine exhaust gases, catalyst warm-up occurs more rapidly when the engine operates under heavier loads and when the catalyst is positioned closer to the engine. Longer periods of vehicle inactivity and lower ambient air temperatures increase the heating required for the catalyst to reach effective operating temperatures, and thus prolong the period of elevated exhaust emission rates. When a vehicle is fully warmed up and the engine and emission controls have reached high temperatures, a vehicle is said to be in hot stabilized operating mode. The excess emissions that result from limited control system effectiveness during cold-start operation are referred to as incremental start emissions.

According to current motor vehicle emission inventories, vehicle starts are responsible for a large fraction of total vehicle emissions. California's MVEI 7F model estimates that incremental start emissions contributed about one-third of the HC and CO, and one-fourth of the NO<sub>x</sub> emitted from light-duty vehicles in the Los Angeles area during the summer of 1991.<sup>4</sup> In the winter, when ambient air temperatures are lower, vehicle starts are estimated to contribute an even larger fraction of total emissions. However, emissions estimates of MVEI 7F and earlier models are uncertain.<sup>5–8</sup> Singer and Harley<sup>8</sup> combined remote sensing measurements of CO emissions from ~70,000 Los Angeles area vehicles with fuel sales data to show that MVEI 7F understated stabilized CO emissions by a factor of ~2 for the summer of 1991. If the stabilized CO inventory is increased by this factor, the estimated contribution of start emissions is reduced to ~18%. In the newer MVEI 7G model, both stabilized exhaust and incremental start emissions estimates are higher than corresponding MVEI 7F values. According to MVEI 7G, incremental start emissions contributed ~29% of CO emissions in the Los Angeles area during the summer of 1991.<sup>9</sup> At present, both the absolute magnitude and relative importance of incremental start emissions remain uncertain.

The objectives of this study were (1) to measure incremental cold-start emission factors from a large sample of in-use vehicles under real-world conditions, and (2) to compare the measured emission factors with MVEI 7G model predictions.

## APPROACH

Inventories of cold-start emissions are calculated as the product of start emission factors, expressed as excess grams of each pollutant emitted per start, and the total number of starts per day for the vehicle fleet. Incremental start emission factors used by 7F and earlier versions of the MVEI model are derived from the dynamometer testing of recruited in-use vehicles on standardized cold start and hot stabilized driving cycles. Emissions are measured in gram/mile units and multiplied by the total distance driven during the tests. For MVEI 7G, start emission factors are derived from cold-start dynamometer tests. Controlled dynamometer testing reduces the effects of many variables, such as driver behavior, which can affect emissions. However, since dynamometer testing is expensive and time-consuming, only limited numbers of vehicles may be tested. Dynamometer testing also requires the voluntary participation of vehicle owners; this can result in sampling bias if owners of high-emitting vehicles are less willing to participate.

As an alternative to dynamometer studies, cold-start emissions can be measured under real-world conditions by sampling the exhaust air in enclosed or underground parking garages.<sup>6</sup> Parking garage studies are “real-world” because emissions are measured from vehicles as they are driven under everyday conditions. In garages used for workday parking, stabilized emissions can be measured as vehicles enter in the morning, and cold-start emissions can be measured as vehicles start and exit in the afternoon. The incremental, or excess, emissions associated with vehicle starting are calculated by difference.

Vehicle emissions may be normalized to miles traveled by measuring the total distance driven by all vehicles inside the garage, and the airflow rates of the garage ventilation system.<sup>6</sup> One problem with this approach is that gram-per-mile emissions vary significantly with engine load. If vehicles spend more time idling during afternoon periods—when cars are started and allowed to warm up for a short time—than during morning periods, differences between morning and afternoon gram-per-mile emission factors may not be due solely to cold-start effects.

By carbon balance, vehicle emissions may also be normalized to fuel consumption, as follows:

$$E_p = \left( \frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO] + \Delta[VOC]} \right) \times \left( \frac{w_c}{12} \rho_f \right) \times M_p \quad (1)$$

where  $E_p$  is the emission factor for pollutant  $P$ ,  $\Delta[P]$ ,  $\Delta[CO_2]$ ,  $\Delta[CO]$ , and  $\Delta[VOC]$  represent the background-corrected

pollutant concentrations measured inside the garage,  $M_p$  is the molecular mass of pollutant  $P$ ,  $w_c$  is the weight fraction of carbon in gasoline, and  $\rho_f$  is the fuel density. Since emission factors are calculated by ratio to total carbon, airflow and driving distance measurements are not required, and uncertainties associated with these measurements are removed from emission factor calculations. Emission factors normalized to fuel consumption are also more consistent as driving varies.<sup>8,10-12</sup> As a result, small changes in driving patterns between morning and afternoon periods should not bias the calculation of incremental start emission factors.

## EXPERIMENTAL

Vehicle emissions were measured during March 1997 in a three-level underground parking garage at an office building in Oakland, CA. The first underground level of the garage accommodates visitor and company vehicles, which enter and exit throughout the day. The bottom two levels (2 and 3) are used for employee parking. Most vehicles were parked on these levels before 9:00 a.m. and remained in the garage until after 4:00 p.m., providing a large sample of cold-starting vehicles in the afternoon period. All vehicle activity and emissions measurements described in this study pertain only to levels 2 and 3 of the garage. Each parking space on these levels is assigned to an individual employee; as a result, vehicles proceed directly to their assigned spaces on these levels. The posted speed limit in the garage is 5 mph.

Morning and afternoon sample periods were chosen to coincide with periods of maximum vehicle activity and the highest pollutant concentrations in the garage, generally from 7:15–8:45 during morning periods, and 16:30–18:00 during evening periods. Exact sampling times varied slightly from day to day; dates and times of all sampling periods are provided in Table 1. Pollutant concentrations and vehicle activity were also monitored directly preceding and following the periods noted in Table 1.

The number of vehicles entering and exiting the garage was recorded during each 10-min interval for all sample periods. All vehicles entering the garage were assumed to be in hot stabilized mode. Departure and arrival times for each vehicle were matched to determine the length of time vehicles were parked before exiting the garage during the afternoon sampling period. The model year and fuel type of each vehicle were determined from vehicle registration records. Typical vehicle trip times during morning and

afternoon periods were measured using a stopwatch. Timing of an arrival trip started as the vehicle turned the corner from the ramp to enter a level and ended when the vehicle was turned off. Departure trips extended from the first crank of the engine until the vehicle reached the exit ramp between levels 1 and 2 of the garage. Vehicle speeds were estimated by visual observations and by measuring the distance traveled during the timed vehicle trips.

During sampling periods, clean ventilation air was supplied to the garage through a single plenum near the center of level 3; background pollutant concentrations were measured by inserting a sample line into this plenum. Polluted garage air was collected through ducts at the east end

**Table 1.** Average pollutant concentrations measured in the garage exhaust air (garage) and ventilation intake air (Bkg) during each sample period.

Date	Location	Time	CO <sub>2</sub> (ppm)	CO (ppm)	NO <sub>x</sub> (ppb)	CH <sub>4</sub> (ppm)	NMHC (ppmC)
<b>Morning Sample Periods</b>							
11-Mar	Garage	7:20-9:00	558	8.3	268	N/A <sup>a</sup>	N/A <sup>a</sup>
11-Mar	Bkg	7:20-9:00	411	0.8	88	N/A <sup>a</sup>	N/A <sup>a</sup>
12-Mar	Garage	7:10-9:00	558	7.4	273	2.37	3.65
12-Mar	Bkg	7:00-9:00	422	0.6	96	2.00	0.31
13-Mar	Garage	7:20-9:00	596	8.3	374	2.33	4.15
13-Mar	Bkg	7:12-9:02	450	1.8	172	2.13	0.56
17-Mar	Garage	7:20-8:50	566	8.7	239	2.12	4.07
17-Mar	Bkg	7:20-8:50	399	0.9	86	2.00	0.33
18-Mar	Garage	7:15-8:45	571	8.0	267	2.25	3.91
18-Mar	Bkg	7:00-9:00	429	1.0	119	2.12	0.39
19-Mar	Garage	7:10-8:50	606	7.8	349	2.33	3.96
19-Mar	Bkg	7:05-8:50	483	1.7	178	2.16	0.59
<b>Afternoon Sample Periods</b>							
10-Mar	Garage	16:30-18:00	560	23.3	735	N/A <sup>a</sup>	N/A <sup>a</sup>
10-Mar	Bkg	16:30-18:00	404	1.1	99	N/A <sup>a</sup>	N/A <sup>a</sup>
11-Mar	Garage	16:30-18:00	578	28.2	782	2.22	5.55
11-Mar	Bkg	16:30-18:00	388	0.7	79	1.85	0.29
13-Mar	Garage	16:40-18:10	621	28.8	895	2.32	6.98
13-Mar	Bkg	16:15-18:00	384	0.6	76	2.00	0.27
17-Mar	Garage	16:30-18:00	560	22.7	588	2.20	4.64
17-Mar	Bkg	16:00-18:00	381	0.6	55	1.95	0.20
18-Mar	Garage	16:35-18:10	574	26.5	647	2.18	5.65
18-Mar	Bkg	16:15-18:00	384	1.0	60	1.95	0.28
19-Mar	Garage	16:40-18:10	592	25.5	674	2.18	5.75
19-Mar	Bkg	16:15-17:55	407	0.5	90	2.00	0.33

<sup>a</sup>Not available. Samples were not collected for this period.

of levels 2 and 3, channeled into a central plenum, and discharged outdoors. Garage air was sampled at a point ~3 m above the junction of the exhaust airstreams from levels 2 and 3. An additional clean air supply on level 2 and the exhaust ventilation system at the west end of the garage were turned off during all sample periods.

Garage exhaust and clean ventilation airstreams were monitored continuously for CO, CO<sub>2</sub>, and NO<sub>x</sub>. CO<sub>2</sub> concentrations were measured using Thermo Environmental Instruments (TECO, Franklin, MA) model 41H gas filter correlation spectrometers. NO<sub>x</sub> concentrations were measured using TECO model 42 chemiluminescent analyzers. CO in garage exhaust was measured with a TECO model 48 gas filter correlation spectrometer; background CO was measured with a Langan Databear electrochemical CO analyzer (Langan Instruments, San Francisco, CA). Continuous monitoring data were averaged and recorded for each 5-min period between 6:30–9:30 and 15:30–18:30.

Total and speciated HC concentrations were measured by collecting integrated 90-min air samples in 6-L stainless steel canisters using XonTech model 910A continuous flow samplers. Background and garage air samples were analyzed by GC-FID at the Bay Area Air Quality Management District Laboratory in San Francisco (see Reference 15 for details of the analytical technique). Carbonyl samples were collected in parallel with HC canister samples using DNPH-impregnated silica cartridges. The cartridges were eluted with acetonitrile immediately following each sample period and the liquid samples were capped and stored in a refrigerator for ~3 months prior to analysis; the extracted samples were at room temperature for ~3 weeks during this period. Carbonyl samples were analyzed by high-performance liquid chromatography (HPLC) to quantify concentrations of individual aldehydes and ketones.<sup>13,14</sup>

## RESULTS

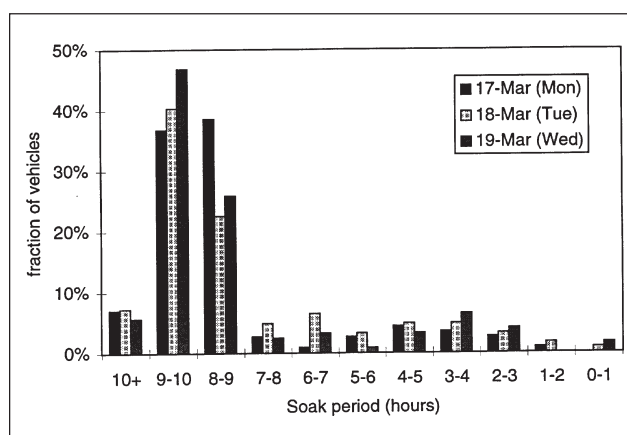
### Vehicle Activity

A summary of vehicle counts during morning and afternoon sampling periods is provided in Table 2. Vehicles entering during the 5–10 min directly preceding emissions sampling are included because these vehicles contributed to pollutant concentrations measured in the garage in the early part of each sample period. Morning vehicle activity was steady from 7:00 until 7:40, increased between 7:40 and 8:00, gradually declined until 8:30, then was steady again until the end of the sample period. During afternoon periods, ~40% of the vehicles exited between 16:30 and 16:50; vehicle traffic then declined gradually through the remainder of each afternoon sample period. Light-duty trucks, minivans, and sport-utility vehicles constituted 25–35% of the vehicle fleet sampled. Almost all of the vehicles sampled had gasoline engines; less than 1% of the vehicles in the garage were diesel-powered. Each

**Table 2.** Vehicle counts during morning and afternoon sample periods.

Date	Day	A.M.: 7:10–8:50			P.M.: 16:20–18:00		
		IN	OUT	% stab <sup>a</sup>	IN	OUT	% stab <sup>a</sup>
10-Mar	Mon	-	-	-	7	110	6%
11-Mar	Tue	128	8	94%	9	120	7%
12-Mar	Wed	123	10	92%	8	137	6%
13-Mar	Thu	-	-	-	8	128	6%
17-Mar	Mon	126	7	95%	5	121	4%
18-Mar	Tue	121	15	89%	7	133	5%
19-Mar	Wed	129	9	93%	11	130	8%
Mean		125	10	93%	8	126	6%

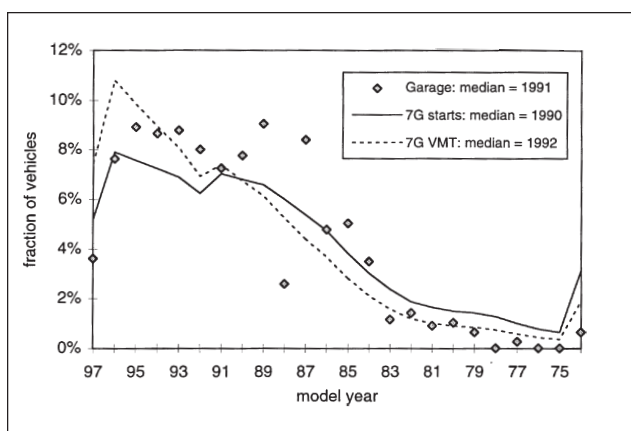
<sup>a</sup>Fraction of vehicles operating in hot stabilized mode.



**Figure 1.** Distribution of soak times for vehicles parked in the garage.

day, 80–90% of vehicles sampled during the afternoon were also present during the morning sample period; the remaining vehicles entered the garage either before 7:10 or after 8:50 a.m. As shown in Table 2, on average 93% of morning vehicles and 6% of afternoon vehicles were operating in hot stabilized mode. About one-third of the vehicles *exiting* the garage in the morning had soak times of less than 1 hr.

Soak time distributions for vehicles exiting between 16:20 and 18:00 on the afternoons of March 17–19 are shown in Figure 1. This figure indicates that 70–80% of vehicles exiting the garage during afternoon periods were parked for 8 hr or more, and fewer than 5% were parked in the garage for less than 2 hr. The age distribution of vehicles parked in the garage during the three-day period is presented in Figure 2, along with the age distributions used by MVEI 7G for 1997 San Francisco Bay Area emission inventory calculations. MVEI 7G uses slightly different age distributions to calculate fleet-average cold start versus stabilized exhaust emissions; both profiles are shown in Figure 2. The age distribution of vehicles parked in the garage is similar to the age distributions used in MVEI



**Figure 2.** Age distributions of vehicles parked in the garage and for the overall Bay Area fleet, as estimated in the MVEI 7G model.

7G. The garage sample includes fewer vehicles from the most recent (1995–1997) and oldest (pre-1983) model years, and a higher fraction of 1984–1993 model year vehicles.

Driving in the garage consisted mainly of low-speed operation at ~10–15 mph. Exit times for vehicles parked on level 2 ranged from 15 to 125 sec, with 90% of the vehicles exiting within 60 sec. A mean exit time of  $41 \pm 3$  sec was calculated from 43 observed trips (vehicles starting from all areas of level 2). Since the layout of the two levels is almost identical, it was assumed that vehicles parked on level 3 followed the same exit pattern as those parked on level 2. Vehicles parked on the lowest level drove through level 2 en route to the garage exit in  $28 \pm 1$  sec. These vehicles spent an additional ~10 sec on the ramp between levels 2 and 3. Therefore, vehicles exiting from level 3 were in the garage for ~80 sec on average following ignition. In the morning, vehicles reached their assigned parking spaces in  $29 \pm 2$  sec after arriving on their assigned level. During morning periods, vehicles parking on level 3 spent  $25 \pm 1$  sec driving through level 2 and an additional ~10 sec on the ramp between levels 2 and 3. Since speeds were similar and no significant traffic back-ups were observed during any morning or afternoon period, these observations confirm that, on average, vehicles spent an additional 10–15 sec in idle during afternoon periods.

### Pollutant Concentrations

Average pollutant concentrations measured during each sample period are presented in Table 1. In this table, methane ( $\text{CH}_4$ ) and nonmethane hydrocarbon (NMHC) concentrations are reported separately. Except for methane, all pollutant levels were much higher in garage exhaust air than in background air. Background pollutant concentrations were similar for most morning and afternoon periods, except on the mornings of March 13 and 19, when background concentrations of  $\text{CO}_2$ , CO,  $\text{NO}_x$ , and NMHC were elevated.  $\text{CO}_2$  levels inside the garage were similar

during morning and afternoon periods. However, after accounting for differences between morning and afternoon background  $\text{CO}_2$  levels,  $\Delta\text{CO}_2$  values were higher during afternoon periods ( $190 \pm 26$  ppm) compared to morning periods ( $144 \pm 14$  ppm). Since ventilation flows and vehicle counts were similar during morning and afternoon periods, the higher  $\Delta\text{CO}_2$  suggests that more fuel was burned per vehicle in the afternoon. This may be attributed to two factors: reduced fuel economy during the period of fuel enrichment at ignition, and the longer vehicle trip times during afternoon periods as compared to morning periods. Garage CO and  $\text{NO}_x$  levels were much higher in afternoon periods as a result of increased emissions of these pollutants during cold start. In contrast, NMHC concentrations in the garage were similar during morning and afternoon periods. While exhaust NMHC emissions were expected to be higher during afternoon periods due to cold start, morning NMHC samples included hot soak evaporative emissions in addition to exhaust emissions.

The composition of volatile organic compound (VOC) (includes both hydrocarbons and carbonyls) emissions measured during morning and afternoon periods is presented in Table 3. The morning profile represents a mix of stabilized exhaust and hot soak evaporative emissions. The afternoon profile represents cold-start exhaust emissions for the garage fleet. The composition of stabilized exhaust VOC emissions measured at the nearby Caldecott tunnel during August 1996<sup>15</sup> is also presented in Table 3. Overall, the garage cold start and tunnel stabilized exhaust profiles are similar. The weight fractions of most compounds are similar in the two profiles, and the same compounds (methane, 2-methylbutane, ethene, toluene, xylene, and MTBE) are most abundant in both profiles. The lower methane and higher acetylene fractions in the cold-start profile are consistent with the reduced catalyst activity expected during cold start.<sup>16–18</sup> However, the acetylene fraction measured in garage cold-start sampling is still much lower than that measured from fleets of non-catalyst vehicles.<sup>17,19,20</sup> Higher abundances of 2-methylbutane and n-butane in garage cold-start samples likely result from the increased presence of these compounds in higher vapor pressure gasoline sold during winter months as compared to the summertime gasoline in use during the Caldecott tunnel study.<sup>21</sup> By contrast, the weight fractions of methylpentanes and n-pentane are higher in the VOC profile measured at the Caldecott tunnel during summer 1996. The cold-start profile indicates a higher ratio of  $\text{C}_7+$  aromatics to benzene compared to stabilized emissions. The increased  $\text{C}_7+$  aromatics to benzene ratio suggests a larger fraction of unburned fuel in the cold-start profile. The combined weight fractions of formaldehyde and acetaldehyde are much lower during

**Table 3.** Measured VOC speciation profiles.<sup>a</sup>

Species	Morning Hot soak + Stabilized Ex. wt% VOC	Afternoon Cold Start Exhaust wt% VOC	Caldecott '96 Stabilized Profile wt% VOC <sup>b</sup>
methane	5.99 ± 2.86	5.37 ± 1.31	9.09 ± 1.25
ethane	0.30 ± 0.17	0.52 ± 0.03	0.92 ± 0.28
propane	0.29 ± 0.06	0.61 ± 0.08	0.12 ± 0.04
n-butane	6.79 ± 1.41	3.18 ± 0.72	1.12 ± 0.13
n-pentane	2.63 ± 0.10	1.83 ± 0.16	2.27 ± 0.18
n-hexane	1.31 ± 0.06	1.33 ± 0.05	1.16 ± 0.10
n-heptane	0.96 ± 0.10	1.02 ± 0.03	0.79 ± 0.09
n-octane	0.62 ± 0.08	0.70 ± 0.04	0.35 ± 0.14
n-nonane	0.20 ± 0.05	0.17 ± 0.02	0.19 ± 0.08
2-methylpropane	1.19 ± 0.34	0.42 ± 0.21	0.28 ± 0.04
2-methylbutane	10.11 ± 0.73	5.91 ± 0.91	8.95 ± 0.80
2-methylpentane	5.32 ± 0.45	4.21 ± 0.18	2.87 ± 0.37
3-methylpentane	3.17 ± 0.23	2.50 ± 0.05	1.70 ± 0.13
2-methylhexane	0.40 ± 0.04	0.42 ± 0.04	0.98 ± 0.09
3-methylhexane	1.08 ± 0.13	1.14 ± 0.08	1.10 ± 0.08
C8+ monosub. alkanes	1.30 ± 0.29	1.48 ± 0.07	0.92 ± 0.10
2,2-dimethylbutane <sup>c</sup>	1.77 ± 0.17	1.19 ± 0.08	0.78 ± 0.06
2,3-dimethylbutane	1.75 ± 0.12	1.13 ± 0.06	0.79 ± 0.31
dimethylpentanes	0.41 ± 0.03	0.37 ± 0.05	0.82 ± 0.07
dimethylhexanes	0.23 ± 0.04	0.27 ± 0.06	0.78 ± 0.28
dimethylheptanes	0.24 ± 0.11	0.26 ± 0.08	0.57 ± 0.10
dimethyloctanes	0.27 ± 0.22	0.22 ± 0.06	0.18 ± 0.02
2,2,4-trimethylpentane	2.11 ± 0.13	2.01 ± 0.07	2.42 ± 0.18
2,3,4-trimethylpentane	1.00 ± 0.07	0.94 ± 0.04	0.81 ± 0.09
cyclopentane <sup>c</sup>	0.46 ± 0.03	0.30 ± 0.02	0.21 ± 0.08
cyclohexane	0.49 ± 0.05	0.48 ± 0.04	0.84 ± 0.07
methyl cyclopentane	2.92 ± 0.16	2.68 ± 0.07	2.38 ± 0.14
methyl cyclohexane	0.54 ± 0.04	0.56 ± 0.19	0.78 ± 0.32
other C5-C9 alkanes	0.41 ± 0.10	0.57 ± 0.18	0.17 ± 0.07
C10+ alkanes	0.47 ± 0.14	0.22 ± 0.06	0.64 ± 0.15
ethene	2.03 ± 0.71	6.02 ± 0.35	5.67 ± 1.04
propene	1.21 ± 0.19	3.20 ± 0.18	3.33 ± 0.43
1-butene/isobutene	1.37 ± 0.32	2.75 ± 0.38	3.43 ± 0.37
c/t-2-butene	0.70 ± 0.14	0.64 ± 0.07	0.64 ± 0.14
1,3-butadiene <sup>d</sup>	0.24 ± 0.05	0.73 ± 0.02	0.45 ± 0.10
1-pentene	0.24 ± 0.17	0.21 ± 0.05	0.13 ± 0.03
c/t-2-pentene	0.39 ± 0.04	0.29 ± 0.05	0.37 ± 0.06
other C5 alkenes	1.00 ± 0.31	0.84 ± 0.15	1.03 ± 0.24
C6+ alkenes	0.75 ± 0.03	0.78 ± 0.08	1.29 ± 0.25
acetylene	1.06 ± 0.11	3.66 ± 0.28	2.64 ± 0.25
benzene	1.44 ± 0.12	2.30 ± 0.11	3.03 ± 0.27
toluene	7.76 ± 0.62	9.20 ± 0.31	7.70 ± 0.32
ethyl benzene	1.12 ± 0.19	1.36 ± 0.04	1.12 ± 0.05
styrene	0.06 ± 0.01	0.19 ± 0.01	0.28 ± 0.04
m/p-xylene	4.75 ± 0.43	5.80 ± 0.22	4.57 ± 0.25
o-xylene	1.96 ± 0.40	2.09 ± 0.07	1.56 ± 0.07
iso- & n-propyl benzene	0.30 ± 0.07	0.31 ± 0.03	0.31 ± 0.04
m/p-ethyltoluene	0.64 ± 0.11	0.77 ± 0.06	1.86 ± 0.08
o-ethyltoluene	0.40 ± 0.14	0.49 ± 0.06	0.33 ± 0.04
1,2,4-trimethylbenzene	1.91 ± 0.34	2.08 ± 0.21	1.50 ± 0.12
1,2,3-trimethylbenzene	0.31 ± 0.15	0.38 ± 0.15	0.22 ± 0.01
1,3,5-trimethylbenzene	0.55 ± 0.20	0.53 ± 0.11	0.00 ± 0.00
diethylbenzenes	0.97 ± 0.50	0.96 ± 0.33	0.38 ± 0.10
other C10+ aromatics	1.07 ± 0.38	1.02 ± 0.26	0.71 ± 0.19
MTBE	8.10 ± 8.31	5.66 ± 0.58	4.96 ± 0.66
formaldehyde	0.41 ± 0.06	0.75 ± 0.01	1.98 ± 0.31
acetaldehyde	0.13 ± 0.02	0.38 ± 0.04	0.33 ± 0.03
other carbonyls	0.51 ± 0.09	0.96 ± 0.19	1.53 ± 0.24
unidentified	3.87 ± 2.16	3.61 ± 2.14	3.36 ± 2.05

<sup>a</sup>Based on analysis of canister samples collected during afternoon periods when 93% of the vehicles were operating in cold start mode.

<sup>b</sup>Mean ± 1 standard deviation of the compound wt% from five sample periods.

<sup>c</sup>2,3-dimethylbutane coeluted with cyclopentane. The peak was resolved to 79% 2,3-dimethylbutane and 21% cyclopentane.

<sup>d</sup>The number shown here is a lower limit; 1,3-butadiene was not stable in the stainless steel canisters.

cold start than during stabilized driving. This difference results from reduced aldehyde production during the fuel-rich period following ignition, and because combustion products are reduced relative to unburned fuel in the cold-start profile. Morning VOC emissions include larger fractions of fuel components such as n-butane, n-pentane, 2-methylpropane, and 2-methylbutane, and smaller fractions of combustion-derived compounds such as ethene, propene, and formaldehyde. These differences are consistent with the presence of hot soak evaporative emissions during morning sampling periods.

Morning NMHC emissions were apportioned to exhaust and evaporative contributions using a chemical tracer approach. This is described by eq 2 below:

$$f_{st} = \frac{w_{i,g}}{w_{i,st}} \quad (2)$$

where  $f_{st}$  represents the fraction of garage NMHC attributable to tailpipe exhaust,  $w_{i,g}$  is the weight fraction of species  $i$  in garage NMHC emissions, and  $w_{i,st}$  is the weight fraction of species  $i$  in stabilized exhaust emissions shown in Table 3. This chemical tracer approach was used only with the combustion-derived species ethane, ethene, acetylene, and propene that are present in exhaust but absent from evaporative emissions. Results of the apportionment are summarized in Table 4, which shows that 33–40% of morning NMHC emissions were attributed to tailpipe sources; the balance was attributed to evaporative sources.

Emission factors were calculated for each sample period using eq 1 and the time-averaged pollutant concentrations from Table 1; these emission factors are shown in

**Table 4.** Apportionment of hydrocarbon emissions to exhaust and evaporative sources.

Tracer Species	wt% NMHC <sup>a</sup>	Exhaust Contribution to Total NMHC <sup>b</sup>				
		12-Mar	13-Mar	17-Mar	18-Mar	19-Mar
Ethene	6.5	42%	13% <sup>c</sup>	36%	41%	36%
Acetylene	3.0	38%	44%	34%	38%	34%
Ethane	1.1	43%	39%	34%	42%	36%
Propene	3.8	35%	32%	29%	34%	29%
Avg.		40%	38% <sup>c</sup>	33%	39%	34%

<sup>a</sup>Weight fraction of species in hot stabilized exhaust emissions measured at Caldecott tunnel in summer, 1996 (see Reference 15).

<sup>b</sup>Fraction of total parking garage NMHC emissions attributed to tailpipe exhaust, estimated using a tracer species and eq 2.

<sup>c</sup>The weight fraction of ethene in VOC measured on March 13 was significantly lower than for all other sampling days; the exhaust contribution to NMHC on this day was calculated using the average results from acetylene, ethane, and propene as exhaust tracers.

Table 5. Typical California Phase 2 reformulated gasoline properties  $\rho_f = 743 \text{ g L}^{-1}$  and  $w_c = 0.85$  were determined from analyses of gasoline samples purchased from all of the major suppliers in the Bay Area during summer 1996.<sup>15</sup> By convention,  $\text{NO}_x$  emission factors were calculated using a molecular mass of  $46 \text{ g mol}^{-1}$ . HC emissions were calculated using a molecular mass of  $14 \text{ g mol}^{-1}$ . Emissions of each pollutant were consistent from day to day, which is expected since many of the same vehicles were measured each day.

Emission factors from morning and afternoon sample periods were extrapolated by linear regression to 0 and 100% hot stabilized driving. The resulting cold start and hot stabilized emission factors, shown in Table 5, differ only slightly from the emission factors measured during afternoon and morning periods. Cold-start emission estimates were further adjusted to account for differences between emission levels averaged over the full cold-start period and those of the first 60 sec (i.e., the period measured in the parking garage), as described below.

**Table 5.** Exhaust emission factors in morning and afternoon sample periods.

Date	CO (g/gal)	NO <sub>x</sub> (g/gal)	NMHC (g/gal)	Stabilized Fraction <sup>a</sup>
<b>Morning Sample Periods</b>				
11-Mar	264	10	N/A	94%
12-Mar	257	11	25	93%
13-Mar	232	12	24	N/A <sup>b</sup>
17-Mar	242	8	19	95%
18-Mar	253	9	25	89%
19-Mar	256	12	24	94%
<b>Afternoon Sample Periods</b>				
10-Mar	673	32	N/A	6%
11-Mar	683	29	65	7%
13-Mar	573	27	68	6%
17-Mar	598	24	60	5%
18-Mar	640	24	68	5%
19-Mar	643	25	70	7%
A.M. mean <sup>c</sup>	251 ± 2	10.3 ± 0.3	23 ± 2	(93 ± 2)%
P.M. mean <sup>c</sup>	635 ± 7	26.8 ± 0.5	66 ± 4	(6 ± 1)%
Stabilized <sup>d</sup>	223 ± 17	8.6 ± 1.3	19 ± 2	100%
Cold start <sup>d</sup>	660 ± 15	27.8 ± 1.2	69 ± 2	0%
Full cold-start period <sup>e</sup>	449	38.6	49	

<sup>a</sup>Fraction of active vehicles in hot stabilized operating mode.

<sup>b</sup>Not available.

<sup>c</sup>Mean ± standard error of morning and afternoon emission factors.

<sup>d</sup>Results of linear regression analysis (see text).

<sup>e</sup>Cold start emission factors adjusted to reflect the average emissions over the full cold-start period, estimated to last for ~200 sec (see text).

## DISCUSSION

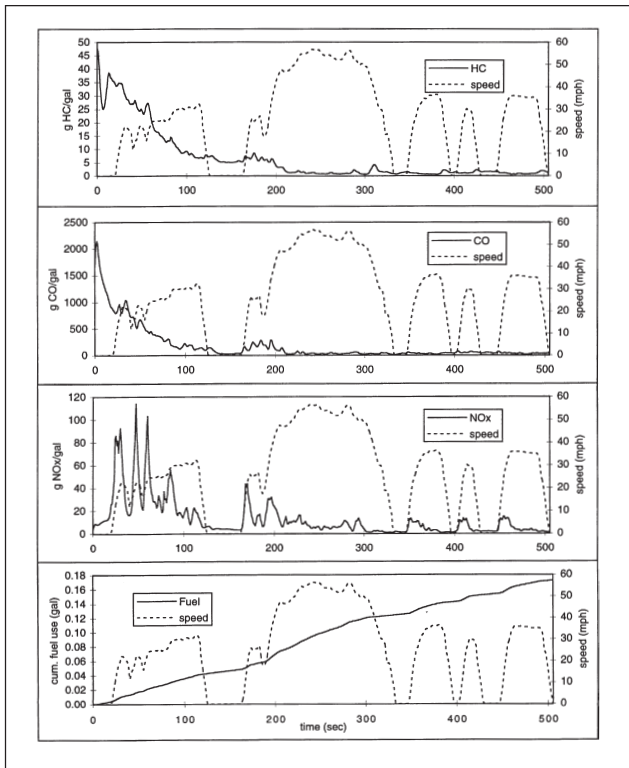
To interpret and use the emissions measurements from the parking garage, more information is required about vehicle operation during cold start. First, it is important to understand how and over what time period the high emissions levels observed during cold start fall to the lower levels characteristic of stabilized operation. With this knowledge, the cold-start emission factors measured in the garage can be related to emissions during the full cold-start period. Second, since one of the objectives of this study is to compare garage results with cold-start emission factors from MVEI 7G, an estimate of the average fuel used during start mode is required (recall that emission factors measured in the garage were expressed in gram-per-gallon units). The ensuing discussion of cold-start emissions, and the estimation of fuel use during cold start, are based on analyses of available dynamometer emissions data.

### Fuel Use During Cold Start

The average second-by-second emissions of 20 1993–1994 model year light-duty vehicles measured during the cold-start portion of the Federal Test Procedure (FTP) are plotted in Figure 3.<sup>22</sup> The gram/gallon emission factors presented in Figure 3 were calculated using eq 1 and exhaust pollutant concentrations measured during each second of the dynamometer test. Although these were not in-use vehicles, their catalytic converters were aged to simulate 30,000–100,000 miles of driving. Prior to testing, vehicles were soaked for a minimum of 12 hr at an ambient temperature of ~70 °F. In Figure 4, catalyst temperature is plotted against time and cumulative fuel use for three of the vehicles; recall that the catalyst must reach operating temperatures of 400–700 °F before significant pollutant conversion occurs.

The FTP cold-start emissions profiles shown in Figure 3 begin with sharp HC and CO peaks that result from fuel enrichment at ignition.  $\text{NO}_x$  emissions remain relatively low during this period (~0–20 sec) even though the catalyst is ineffective. CO and HC emissions drop quickly through the first ~80–100 sec as the catalyst warms rapidly. Catalyst temperature, HC, and CO emissions then remain approximately constant through the extended idle period beginning at ~125 sec. By 200–220 sec, the vehicles' catalysts have reached stable high temperatures and emissions of HC and CO drop to their stabilized values, as shown in Figures 3 and 4. In contrast to the smoother CO and HC profiles,  $\text{NO}_x$  emissions are characterized by sharp peaks which result from each acceleration event. These peaks are highest during the first 80–100 sec, moderate during the acceleration to >50 mph (~165–210 sec), then roughly constant in magnitude after about 210 sec.

Figure 3 shows that while emissions are much higher during cold-start driving than after vehicles have warmed



**Figure 3.** Average second-by-second emissions of 20 1993–1994 model year vehicles tested on FTP cold-start cycle. Data from testing described in Reference 22.

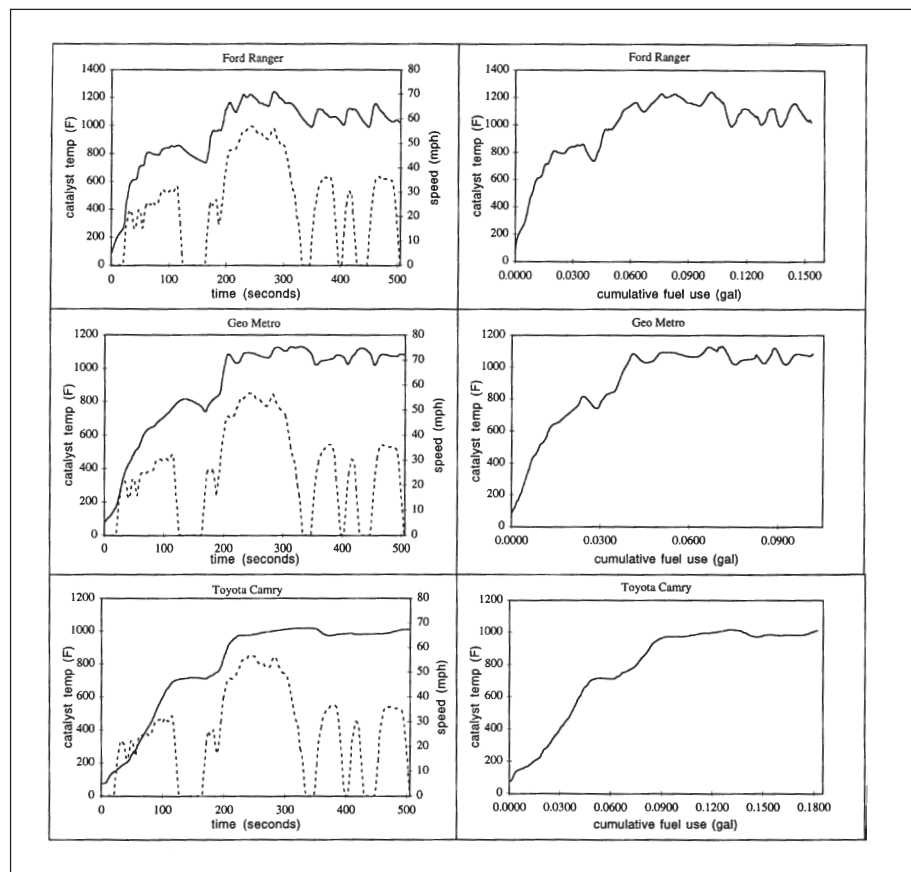
to stabilized operation, there is no single emissions level that persists throughout the cold-start period. It is therefore important to identify clearly the period over which cold-start emissions are averaged.

Figure 4 shows that in the FTP cycle, heating of the catalyst to effective operating temperatures is approximately linearly related to both elapsed time and cumulative fuel use. Results from a recent U.S. Environmental Protection Agency (EPA) study<sup>23</sup> comparing incremental start emissions during the first 298 sec of the CARB LA92 (Unified) cycle and the EPA ST01 cycle suggest that the relationship between catalyst warm-up and fuel use may be independent of the test cycle. The speed versus time trace of the two cycles are plotted in Figure 5a; Figures 5b–5c show the HC and CO emissions versus fuel use for a 1984 Oldsmobile driven through the two cycles. Reductions in HC and CO emissions indicate increasing catalyst effectiveness as

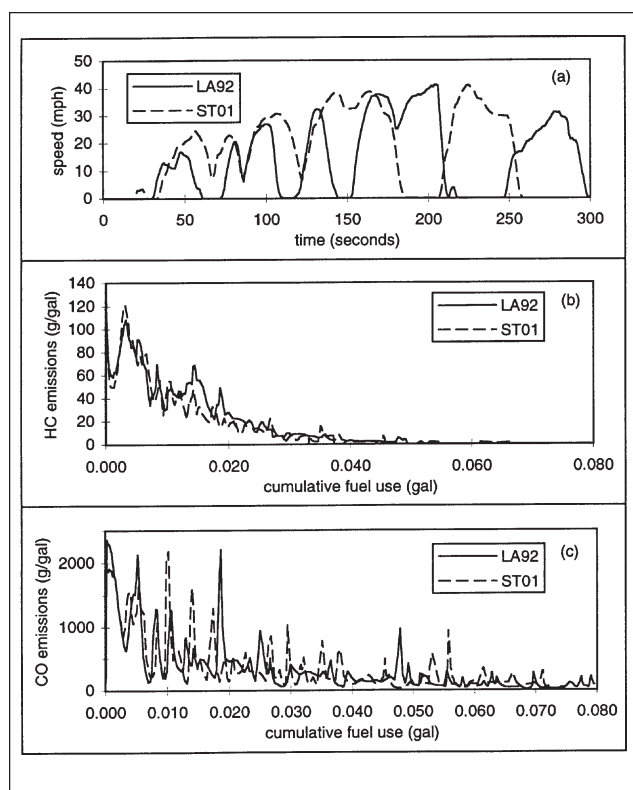
cumulative fuel use increases. By the time that ~0.04 gal of gasoline have been consumed in each test, HC and CO emissions have reached their stabilized levels. While the emissions versus fuel use relationships are similar for the two cycles, it must be noted that the early portions of the two driving cycles are also similar. Each cycle begins with ~30 sec of idle, followed by an acceleration to ~15–25 mph and a deceleration event; Figures 5b–5c show that by the end of this period, emissions have reached very low levels, indicating that much of the catalyst heating has already occurred. Testing of additional vehicles on driving cycles with shorter initial idle periods and different speed traces is needed to examine further the relationship between catalyst heating and fuel use.

### Calculation of Gram/Start Emission Factors

The preceding discussion shows that the cold-start period may be defined by the amount of fuel which must be consumed before stabilized engine and catalyst operating temperatures are reached. If this fuel use is multiplied by the average gram-per-gallon emissions for the same period, an estimate of the total grams of pollutant emitted per start may be calculated. Real-world cold start and hot stabilized emission factors were measured in the parking



**Figure 4.** Second-by-second FTP data described in Reference 22 showing that heating of the catalyst to effective temperatures (400–700 °F) is approximately linearly related to both fuel use and elapsed time.



**Figure 5.** Cold-start data for a 1994 Oldsmobile Achieva tested on EPA ST01 and CARB LA92 cycles: (a) speed versus time; (b) HC emissions versus fuel use; (c) CO emissions versus fuel use. Data from testing are described in Reference 23.

garage and are presented in Table 5. Fuel use was estimated by analyzing a subset of emissions data from California's 12th light-duty vehicle surveillance program.<sup>24</sup> The ongoing surveillance program recruits for emissions testing a sample of California in-use vehicles. Results of the testing provide the basis for emission factors used in the MVEI model. In the present study, second-by-second emissions data were analyzed for 82 in-use vehicles tested on the LA92 driving cycle during 1992. The mean and median model year of the vehicle sample was 1987, the mean odometer reading was 86,000 miles, and ~25% of the vehicles were light-duty trucks. Neither catalyst temperature nor catalyst efficiency were measured during the program; the end of cold start was therefore inferred from the emissions data.

Figure 6 shows the average HC, CO, and NO<sub>x</sub> emission factors of the 82 vehicles during each of the first 850 sec of the LA92 driving cycle. A cumulative plot of average second-by-second fuel use is also included in Figure 6. In contrast to the FTP cold-start test, the early portion of the LA92 cycle includes harder accelerations and more high-speed driving. As a result, emissions data from the LA92 cycle fluctuate more than for the FTP (compare Figures 3 and 6). Nevertheless, Figure 6 shows that, on average, cold-start effects ended after ~200 sec of operation

for the surveillance program vehicles; during this period average fuel use was 0.07 gal.

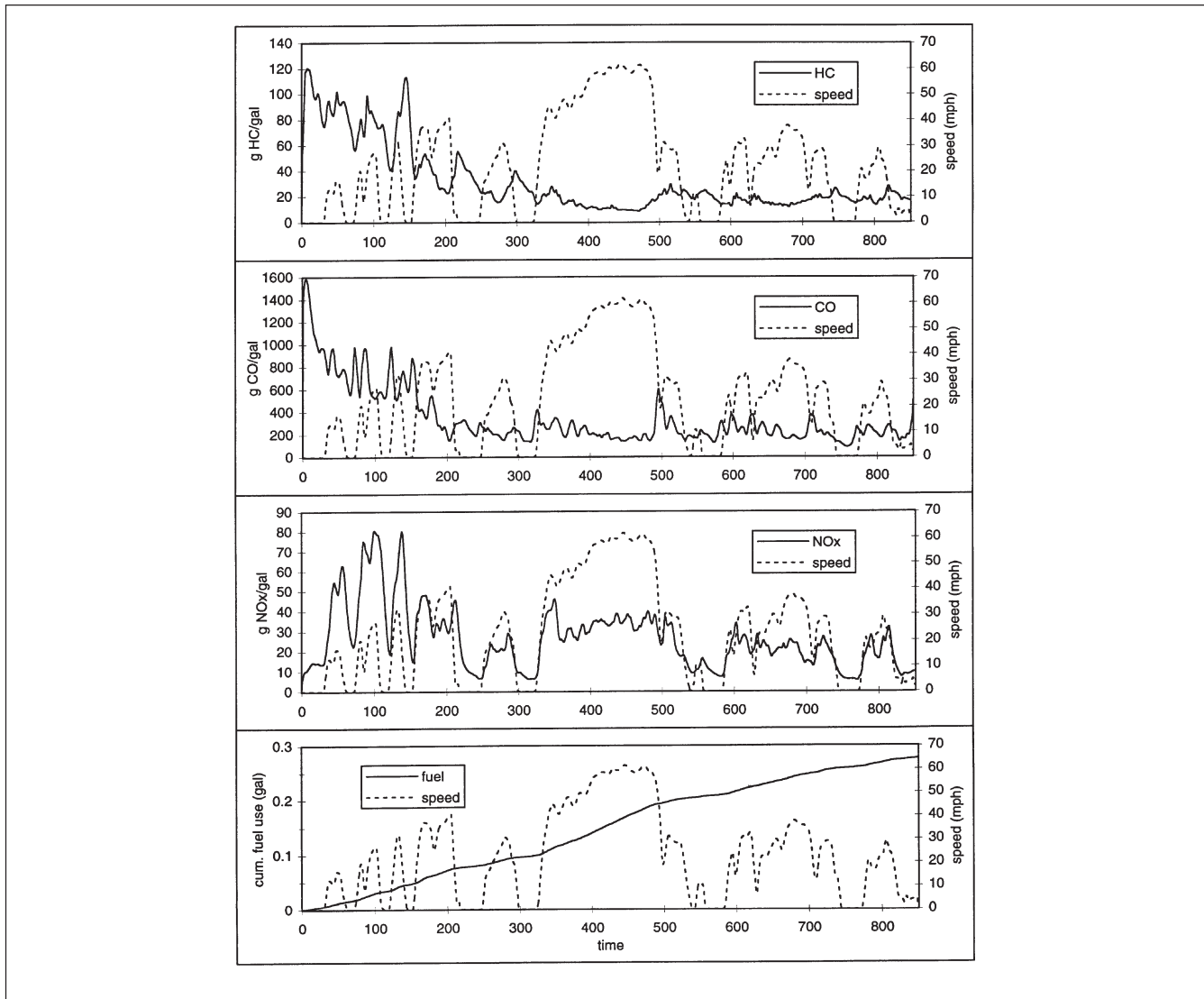
To verify that most of the cold-start effects had occurred within the first 200 sec, stabilized emissions were estimated from a later portion of the driving cycle (550–850 sec) which has a speed versus time trace similar to the first part of the LA92 test. Average emissions during this period were 224 g CO/gal, 17 g HC/gal, and 20 g NO<sub>x</sub>/gal. These stabilized emissions levels are lower than emissions during the 200-sec cold-start period by factors of 3, 4, and 2 for CO, HC, and NO<sub>x</sub>, respectively.

Total excess mass emissions,  $M$ , for the cold-start portion of the cycle were calculated using the following formula:

$$M = \sum_{i=1}^{300} (E_i - E_s) f_i \quad (3)$$

where  $E_i$  and  $f_i$  represent the average instantaneous gram-per-gallon emissions and fuel use of all 82 vehicles measured during each of the first 300 sec, and  $E_s$  was the average stabilized emission level (in g/gal units) measured during the period 550–850 sec. Using this approach, it was verified that 94% of excess HC, 100% of excess CO, and 96% of excess NO<sub>x</sub> emissions occurred during the first 200 sec of operation for the surveillance program vehicle fleet. A similar analysis of the FTP emissions data shown in Figure 3 produces comparable results: 0.07 gal of fuel was used and most of the cold-start effects occurred within the first 200 sec. Analysis of the FTP data also shows that >80% of the excess HC and CO and 70% of the excess NO<sub>x</sub> were emitted during the first 100 sec of the test; during that period only 0.035 gal of gasoline were consumed.

Emission factors measured in the parking garage corresponded to the first ~40 and ~80 sec of operation for vehicles parked on levels 2 and 3, respectively. For the surveillance program vehicles, average emissions during the full 200-sec cold-start period were lower than emissions averaged over the first 60 sec (corresponding to the period over which vehicles were measured in the garage) by factors of 0.71 for HC and 0.68 for CO; average NO<sub>x</sub> emissions during the first 200 sec were *higher* than during the first 60 sec by a factor of 1.39. Cold-start emission factors measured in the garage were scaled by these factors to calculate emission factors representative of the full 200-sec cold-start period; these are shown at the bottom of Table 5. Incremental start emission factors were calculated as the difference between full cold-start emission levels and the stabilized emission levels presented in Table 5. Incremental start emission factors (in g/gal units) were then combined with the estimated cold-start fuel consumption of 0.07 gal to calculate exhaust emission factors of 2.1 g NMHC, 16 g CO, and 2.1 g NO<sub>x</sub> per vehicle start.



**Figure 6.** Average second-by-second emissions of 82 light-duty vehicles tested on CARB LA92 cycle. Data from testing are described in Reference 24.

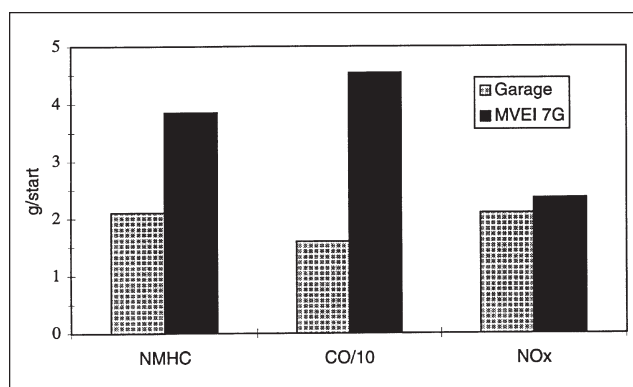
### Comparison to MVEI 7G

Figure 7 compares the gram/start emission factors derived from parking garage measurements to MVEI 7G model estimates for a catalyst-equipped fleet of 70% cars and 30% light-duty trucks. The MVEI 7G model was run for summer 1997 conditions to reflect the ambient air temperatures of ~65–75 °F at which vehicles soaked in the garage. The distribution of soak times measured in the garage also was specified for the model runs. MVEI 7G cold-start emission factors are higher than those derived from parking garage measurements by factors of 1.8 for NMHC and 2.8 for CO, whereas MVEI 7G NO<sub>x</sub> emission factors are comparable to those derived from parking garage measurements. This suggests that the absolute magnitude of incremental cold-start NMHC and CO emissions may be overstated in current emission inventories. When combined with previous studies which have shown that hot stabilized HC and CO emissions may be significantly understated, the results of this study suggest that

the importance of cold starts as a fraction of total on-road vehicle emissions of HC and CO may be substantially overstated in current emission inventories.

### CONCLUSIONS

This study demonstrates the use of underground parking garages for the measurement of cold-start emissions from large samples of in-use vehicles. Cold-start emission factors of  $69 \pm 2$  g NMHC/gal,  $660 \pm 15$  g CO/gal, and  $27.8 \pm 1.2$  g NO<sub>x</sub>/gal were measured during the first ~40–80 sec of vehicle operation in a parking garage in Oakland, CA, during March 1997. Average fuel consumption during start mode was estimated to be 0.07 gal, based on an analysis of second-by-second emissions data from California's light-duty vehicle surveillance program. Incremental start emission factors of 2.1 g NMHC, 16 g CO, and 2.1 g NO<sub>x</sub> per start were derived from the fuel use estimates and the emissions measured in the garage. These emission factor estimates are lower than MVEI 7G estimates by 45% for



**Figure 7.** Comparison between incremental start emission factors calculated from garage measurements and predictions of the MVEI 7G model.

NMHC, 65% for CO, and 12% for NO<sub>x</sub>. It appears that both the absolute magnitude and relative importance of cold-start CO and HC emissions may be overstated in current vehicle emission inventories.

#### ACKNOWLEDGMENTS

The authors thank Mike Traverse and Grahams Scovell of the Bay Area AQMD for their assistance in preparing the air monitoring instruments; Chris Gee and Waymond Chan, retired from the BAAQMD, for their input regarding flow calibration methods; Tom Wenzel of Lawrence Berkeley National Laboratory for providing the surveillance program data; David Brzezinski of the EPA for providing the EPA cold-start testing data; Feng An of UC—Riverside for helpful comments and insights about cold-start emissions; Kochy Fung and Kent Hoekman for providing the carbonyl analyses; and Bill Kerr and his staff at the parking garage. This research was supported primarily by the University of California Transportation Center. Additional support was provided by Chevron.

#### REFERENCES

1. Calvert, J.G.; Heywood, J.B.; Sawyer, R.F.; Seinfeld, J.H. "Achieving acceptable air quality: Some reflections on controlling vehicle emissions," *Science* **1993**, *261*, 37-45.
2. Heywood, J.B. *Internal Combustion Engine Fundamentals*; McGraw-Hill: New York, 1988.
3. An, F.; Barth, M.; Scora, G.; Younglove, T. "Catalyst cold-start characterization and modeling." Presented at the Sixth CRC On-Road Vehicle Emissions Workshop, San Diego, CA, 1996.
4. "Predicted California On-Road Motor Vehicle Emissions (BURDEN7F)"; Mobile Source Emission Inventory Branch. California Air Resources Board: Sacramento, CA, 1993.
5. Fujita, E.M.; Croes, B.E.; Bennett, C.L.; Lawson, D.R.; Lurmann, F.W.; Main, H.H. "Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO<sub>x</sub> in California's South Coast Air Basin," *J. Air & Waste Manage. Assoc.* **1992**, *42*, 264-276.
6. Ingalls, M.N.; Smith, L.R.; Kirksey, R.E. *Measurement of On-Road Vehicle Emission Factors in the California South Coast Air Basin: Regulated Emissions*; Southwest Research Institute: San Antonio, TX, 1989; Vol. 1.
7. Pierson, W.R.; Gertler, A.W.; Bradow, R.L. "Comparison of the SCAQS tunnel study with other on-road vehicle emission data," *J. Air & Waste Manage. Assoc.* **1990**, *40*, 1495-1504.
8. Singer, B.C.; Harley, R.A. "A fuel-based motor vehicle emission inventory," *J. Air & Waste Manage. Assoc.* **1996**, *46*, 581-593.
9. "MVEI 7G"; Version 1.0, Technical Support Division. Mobile Source Emission Inventory Branch. California Air Resources Board: Sacramento, CA, 1996.

10. Ashbaugh, L.L.; et al. "On-road-remote sensing of carbon monoxide and hydrocarbon emissions during several vehicle operating conditions." Presented at the Air & Waste Management Association/EPA Conference on PM10 Standards and Nontraditional Particle Source Controls, Phoenix, AZ, 1992.
11. Stedman, D.H.; Bishop, G.A.; Beaton, S.P.; Peterson, J.E.; Guenther, P.L.; McVey, I.E.; Zhang, Y. "On-Road Remote Sensing of CO and HC Emissions in California"; final report to the California Air Resources Board, Contract No. A032-093; University of Denver: Denver, CO, 1994.
12. Pierson, W.R.; Gertler, A.W.; Robinson, N.F.; Sagebiel, J.C.; Zielinska, B.; Bishop, G.A.; Stedman, D.H.; Zweidinger, R.B.; Ray, W.D. "Real-world automotive emissions – Summary of recent tunnel studies in the Fort McHenry and Tuscarora Mountain tunnels," *Atmos. Environ.* **1996**, *30*, 2233-2256.
13. Fung, K.; Grosjean, D. "Determination of nanogram amounts of carbonyls as 2,4-dinitrophenylhydrazones by high-performance liquid chromatography," *Anal. Chem.* **1981**, *53*, 168-171.
14. Fung, K., Atmospheric Assessment Associates, Inc., Calabasas, CA. Personal communication, 1997.
15. Kirchstetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Hesson, J.M. "Impact of California reformulated gasoline on motor vehicle emissions: 2. Volatile organic compound speciation and reactivity," *Environ. Sci. Technol.* **1999**, *33*, 329-336.
16. Lonneman, W.A.; Seila, R.L.; Meeks, S.A. "Non-methane organic composition in the Lincoln tunnel," *Environ. Sci. Technol.* **1986**, *20*, 790-796.
17. Jackson, M.W. "Effect of catalytic emission control on exhaust hydrocarbon composition and reactivity," SAE Technical paper no. 780624, Society of Automotive Engineers, Warrendale, PA, 1978.
18. Black, F.M.; High, L.E.; Lang, J.M. "Composition of automobile evaporative and tailpipe hydrocarbon emissions," *J. Air Pollut. Control Assoc.* **1980**, *30*, 1216-1221.
19. Lonneman, W.A.; Kopczynski, S.L.; Darley, P.E.; Sutterfield, F.D. "Hydrocarbon composition of urban air pollution," *Environ. Sci. Technol.* **1974**, *8*, 229-236.
20. Harley, R.A.; Hannigan, M.P.; Cass, G.R. "Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere," *Environ. Sci. Technol.* **1992**, *26*, 2395-2408.
21. Cleary, K.; Brisby, S.; Jennings, T. "Proposed Amendments to the California Phase 2 Reformulated Gasoline Regulations, Including Amendments Providing for the Use of a Predictive Model"; staff report, California Air Resources Board: Sacramento, CA, 1994.
22. Data on Supplemental FTP Emissions Database CD-ROM, available from Office of Mobile Sources, U.S. Environmental Protection Agency. Testing described in: Haskew, H.M.; Cullen, K.; Liberty, T.F.; Langhorst, W.K. "The execution of a cooperative industry/government exhaust emission test program." Presented at the 1994 Convergence International Congress on Transportation Electronics, Dearborn, MI, 1994; SAE paper no. 94C016.
23. Enns, P.; Brzezinski, D. *Comparison of Start Emissions in the LA92 and ST01 Test Cycles*; U.S. Environmental Protection Agency. Assessment and Modeling Division. Office of Mobile Sources: Ann Arbor, MI, 1997; M6.STE.001.
24. Devesh, S. "Test Report of the Light-Duty Vehicle Surveillance Program"; Series 12 (LDVSP 12); Mobile Source Division. California Air Resources Board: El Monte, CA, 1994. MS-94-04.

#### About the Authors

Brett Singer recently completed his Ph.D. in the Department of Civil and Environmental Engineering at the University of California at Berkeley. He is currently a postdoctoral researcher at Lawrence Berkeley National Laboratory. Brett has an M.S. degree in environmental engineering from UC Berkeley and a B.S. degree in mechanical engineering from Temple University. Rob Harley is an Associate Professor in the Department of Civil and Environmental Engineering at UC Berkeley. He holds M.S. and Ph.D. degrees in environmental engineering science from Caltech, and a B.S. degree in engineering science from the University of Toronto. Please direct correspondence to Rob Harley, Department of Civil and Environmental Engineering, 631 Davis Hall #1710, University of California, Berkeley, CA 94720-1710.