Second-by-Second Characterization of Cold-Start Gas-Phase and Air Toxic Emissions from a Light-Duty Vehicle

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ABSTRACT

Tailpipe pollutants from motor vehicles are linked to environmental concerns and human health issues. Initial ignition of a gasoline engine requires fuel-enriched conditions that produce a significant portion of trip emissions. Few studies to date have quantified the exhaust air toxics emissions for light-duty vehicles during cold start, the focus of this study. Real-world tailpipe emissions were measured from a 1999 Toyota Sienna minivan with an innovative on-board measurement system. A Fourier Transform Infrared (FTIR) Spectrometer was used to measure 27 gas-phase and mobile source air toxic (MSAT) emissions for cold start, extended idle, and warm-up driving at one-second temporal resolution. Analysis demonstrated that (a) time to optimal function of emissions control devices could not be indicated by one species, as it varied for different pollutants; (b) extended idle conditions following cold start produced elevated emissions for MSAT species as compared to warm-up driving; (c) peak concentrations for species from each emission category were affected by ambient temperature, ranging from 9.5 to 38.4 °C, with the exception of carbon dioxide. Carbon monoxide produced peak emissions three orders of magnitude higher than hot-stabilized conditions for an average of 90 seconds, regardless of operation conditions, while nitric oxide peak emissions were over an order of magnitude higher during warm-up driving than extended idle. Peak MSAT emissions, up to two orders of magnitude higher than hot-stabilized idle, were maintained or increased during extended idle and decreased to baseline within 100 to 200 seconds of warm-up driving.

INTRODUCTION

Vehicle emissions have widely known adverse environmental and human health effects, resulting from regulated and unregulated pollutant byproducts of fuel combustion. Mobile source air toxics (MSATs) are of particular interest, as they are identified as cancer-causing agents or potentially harmful to human health [1]. Further, vehicle emissions models are predominantly informed by laboratory testing at baseline conditions, neglecting the influence of real-world conditions on engine operation and resulting emissions. Recent work to improve inventories and enhance the accuracy of emissions models has created a need for real-world data collection.

The data analyzed here were collected as part of a pilot study monitoring both particulate and gaseous emissions of real-world vehicles in northern climates, in line with the research aims of the Transportation Research Center at the University of Vermont. The overall objectives of this broader research are (a) to better characterize tailpipe emissions during real-world operation of vehicles on a second-by-second basis; (b) to speciate tailpipe exhaust from alternative vehicles operating under variable terrain conditions in a seasonal climate, with specific focus on unregulated compounds. The focus of this study is gas-phase emissions with particular attention on four of the recognized MSAT species during cold starts, an area that has received relatively little attention. This is surprising given that initial ignition of a gasoline engine from cold start requires fuel-enriched conditions that are known to produce a significant portion of trip emissions because the vehicle's exhaust aftertreatment (catalytic converter) is not yet warmed to operating temperature.

Real-world studies have utilized portable emissions measurement systems (PEMS) to quantify tailpipe emissions while vehicles are in operation on the road network [2-9]. Portable systems are advantageous over dynamometer laboratory tests for understanding the emissions resulting from real-world driving conditions. Many PEMS measure a small selection of emissions, limited to species regulated by Environmental Protection Agency emissions certification standards [4, 8]. Other researchers have instrumented vehicles to develop more comprehensive speciation of emissions, implementing Fourier Transform Infrared Spectrometers (FTIR) to analyze real-world gas-phase emissions [2, 3, 5-7, 9]. Though the PEMS employed by these institutions are capable of characterizing MSAT emissions [7, 9], only one group has pursued quantifying these over on-road, cold start driving cycles [6]. Additionally, low-emitting vehicles (typical of the most recent model year vehicles) require instrumentation capable of lower detection limits, compelling development of new PEMS systems. This study investigates use of FTIR for on-board tailpipe emissions, alongside particle sizing and counting instrumentation (see [10])

Effects of variable terrain [11] and seasonal climate temperature ranges [12-16] influence the operation of vehicles, as passenger cars are designed to operate at maximum efficiency within typical temperature and terrain ranges. Second-by-second emissions measurements allow the transient effects encountered in real-world driving scenarios to be analyzed. To date, only temporal resolution significantly greater than one second have been achieved for FTIR on-board emissions quantification [7, 9], creating a need for higher temporal resolution real-world emissions data.

Pollutant concentrations emitted from the tailpipe of vehicles during cold starts is considerably higher than during travel, even with the influence of peaks occurring during on-road events [2]. Ambient temperature is known to play a significant role influencing cold start emissions [12, 14-16]. The enriched conditions following initial ignition of the engine produce high concentrations of hydrocarbons and carbon monoxide, which is amplified by colder conditions, as more fuel is required for colder, higher density, air combustion [13]. Additionally, warm-up driving patterns immediately following engine ignition (after 12-hour cold soak) affect the total level of emissions produced from cold starts. Speciation of cold start exhaust in laboratory settings at varied temperatures based on real-world driving cycles has been reported, but little consideration has been paid to quantifying unregulated species for cold starts with an on-board system [6]. Moreover, a significant gap in the literature exists in characterizing gaseous and particulate cold start emissions simultaneously during real-world, on-road warm-up driving. Groups conducting similar research have reported solely on gaseous cold start emissions from light-duty gasoline vehicles and found benzene, toluene, xylenes, and formaldehyde to be the dominant species [6]. Toluene and xylene had elevated emissions at engine start, whereas benzene and formaldehyde reached peak emissions further into the driving cycle [6].

METHODOLOGY

A 1999 Toyota Sienna minivan was instrumented with the Total On-Board Tailpipe Emissions Measurement System (TOTEMS) developed by researchers at the University of Vermont and discussed in detail in a separate papers (TRB 10-3023; [17]). The

instrumentation was utilized in a single vehicle as a proof of concept pilot study [18]. The vehicle was equipped with a 3.0-liter V6 engine and was rated as a low-emission vehicle (LEV) according to California Air Resources Board (CARB) Executive Order A-14-351. The specific model used in the study had an odometer reading of over 140,000 miles and was fueled with unleaded 87-octane gasoline from Gulf Oil L.P.

Here, the pilot study cold start gas-phase emissions data for six days of sampling are analyzed in detail. Cold start was defined by an engine soak time of at least 12 hours prior to engine ignition. Particle number distributions for these cold starts are presented in a separate paper (TRB 10-3038; [10]).

TOTEMS Instrumentation

TOTEMS is a portable emissions measurement system capable of measuring vehicle position, ambient conditions, engine operation, exhaust flow rate, exhaust temperature, and gas-phase and particle number tailpipe emissions at one-hertz resolution while operating over real-world driving scenarios. Detailed information on the full suite of TOTEMS instruments is presented in a separate paper (TRB 10-3023; [17]). Below, the key aspects of gas-phase emissions measurement are described.

Power Supply

Instrumentation was powered by two Lifeline absorbent glass mat (AGM) lead-acid batteries rated to 12 volts and 255 Amp-hours. These batteries deliver the power necessary to run TOTEMS through a Vector 2500-watt power inverter. The system avoids utilizing the vehicle as a power source to prevent artificial load on the engine, in turn affecting emissions.

Vehicle Behavior

Data from the vehicle computer was acquired through an AutoEnginuity ScanTool OBD-II Connector. The scantool communicates with the vehicle to collect second-by-second operational parameters, including engine rotations per minute (RPM), vehicle speed, engine load, and mass-air-flow (MAF). In addition to the scantool, accelerations in three dimensions were recorded by the Crossbow accelerometer. The unit was positioned on the roof of the car with the x-axis in line with forward motion of the vehicle, y-axis lateral motion, and z-axis vertical motion.

Ambient Conditions

Onset HOBO loggers acquired ambient temperature and relative humidity during sampling. The instrumentation system performance may be influenced by temperature; therefore, a second temperature and relative humidity logger was placed within the vehicle to monitor TOTEMS surrounding conditions.

Tailpipe Adapter and Exhaust Parameters

A custom-built tailpipe adapter was affixed to the end of the tailpipe of the test vehicle. The adapter extends the factory tailpipe to house: (i) ports for sampling exhaust parameters, (ii) a pitot tube, and (iii) an exhaust sampling probe. A Type J thermocouple measured exhaust temperature. A pitot tube and differential pressure transducers measured static and dynamic pressure of the exhaust for conversion to exhaust flow rate based on laboratory calibration equations for the pitot tube [18]. A perforated stainless

steel sampling probe extended perpendicular through the tailpipe adapter for delivery of exhaust samples to on-board emissions instrumentation. Samples were transferred into the vehicle through an Atmoseal smooth-walled flexible stainless steel heated line maintained at 191°C. Maintaining a high exhaust temperature sample prevented nucleation of particles before mixing with dilution air for particle analysis and maintained the sampling temperature necessary for gaseous species analysis.

Fourier Transform Infrared Spectrometer

A MKS Instruments MultiGas 2030 High-Speed Fourier Transform Infrared Spectrometer (FTIR) was used to characterize the gaseous emissions from the tailpipe of the Toyota Sienna minivan. The FTIR instrument simultaneously quantified 27 species from the exhaust of the vehicle at one-second resolution. Quantification for each compound was based upon manufacturer calibrations, internal to the MultiGas 2000 software package. Exhaust composition was determined by analysis of infrared spectra. The manufacturer calibrations and exhaust composition guidelines were assumed accurate for the purpose of this analysis. Independent procedures to verify the manufacturer calibrations and method of exhaust speciation for gasoline exhaust complex mixtures are under development at the University of Vermont. Prior to the pilot study data collection, MultiGas response was verified using a calibration emissions mix of carbon monoxide, carbon dioxide, nitric oxide, and a typical hydrocarbon surrogate, propane in a nitrogen balance. Tabulated in TABLE 1, the emissions mix certified concentrations were reasonably comparable to the resulting FTIR concentrations. The largest discrepancy between the certified mix and the MG2030 reported concentration was for carbon dioxide, at about a 10% difference.

TABLE 1 Percent difference between FTIR response and certified emissions mix concentrations for select compounds

Compound (unit)	Concentrations		Percent Difference
	Emissions Mix	MKS MG2030	
CO (%)	8.04	7.98	-0.75
CO_2 (%)	12.22	10.94	-10.47
NO (ppm)	3030	3134.93	3.46
C_3H_8 (ppm)	3230	3120.38	-3.39

The MultiGas instrument has a wavelength resolution of 0.5 cm^{-1} and a path length of 5.11 meters, capable of 5 Hz data recording. A flow rate of 12 liters per minute through the FTIR was used to achieve one-second sample residence time in the sample cell. Second-by-second resolution data enables analysis of the relationships between transient vehicle operation and resulting emissions. A slower rate of record, achieved by others utilizing similar methodologies but different instruments, may not capture the variability that driver behavior may induce on the engine operation and resulting tailpipe exhaust composition.

Sample flow through the MultiGas 2030 HS was filtered of particles to prevent damage to internal components (gold-plated mirrors and potassium bromide windows within the sample cell can accumulate particulate or be attacked by water, respectively; both interfere with analysis). To protect the sample cell, the inlet of the FTIR was fixed with a 2.0-micron particulate filter certified for particle mass measurements in line with a 0.1-micron cartridge filter. The series of filters were insulated to ensure minimal heat loss across the stainless steel housings. Maintenance of the high temperatures prevented water condensation that could potentially change the composition of exhaust prior to analysis. It should be noted that the MultiGas instrument quantifies water vapor with each analysis point.

A personal sampling pump was chosen to draw the necessary 12-liter per minute raw exhaust flow through the gas-phase measurement system at 191°C. Typical personal sampling pumps have their own rechargeable battery power source, preventing additional load on TOTEMS power supply system. The SKC Leland Legacy pump provides adjustable 10 to 15 liters per minute flow rate, with up to 24 hours of operational time on one charge. Two water traps precede the pump to prevent water damage or flow obstruction.

Compound Quantitation Limits As each exhaust emissions species was quantified according to a distinct calibration dataset, the minimum concentration detection limits for the instrument are defined on an individual compound basis. The manufacturer specifies the calibration ranges and approximate accuracy of measure for each compound; however, sampling detection limits vary according to sampling rate. The goal of TOTEMS was to achieve the lowest detection limit possible for one-second temporal resolution exhaust measurements. Individual compound detection limits for the FTIR were determined based on tunnel blank data collected before every run. Tunnel blanks were routinely collected as a part of the quality assurance and quality control (QA/QC) procedure, from the flow of ambient air through the exhaust pipe and transfer lines while the vehicle's engine was off. Conceptually, these ambient air measurements provided a background measure and three times the standard deviation of tunnel blank average concentration was defined as the individual compound's detection limit (TABLE 2). The detection limits reported in TABLE 2 were calculated over four of the sampling run QA/QC procedures. The calculation for carbon monoxide was based on three tunnel blank data sets, as one of the four procedures produced extraneous data for CO possibly due to the influence of vehicles starting in close proximity to the test vehicle during tunnel blank data collection. Maximum concentration limits reported in TABLE 2 are concentrations of the highest calibration standard used to generate the calibration curve for that species obtained from the MKS software. For comparison, the last column of Table 1 shows the concentration range for the 5-gas analyzer that the MultiGas replaced in the on-board measurement system [19]. Note that the MultiGas allows real-time speciation of gases in vehicle exhaust unlike traditional 5-gas analyzers (e.g., hydrocarbons and NOx individual species in TABLE 2). Additionally, a conventional 5-gas analyzer is calibrated to an emissions mix, providing single calibration points for each gas surrogate on which to base measurements from the complex exhaust composition. In contrast, the MultiGas has a range of concentrations, presented in

TABLE 2, used to interpolate the compound concentration in the tailpipe emissions sample.

TABLE 2 Gas Species Detection Limts and Lower and Upper Quantitation Limits for the MKS MultiGas FTIR Instrument

Compound	Detection Limit (ppm or %)	Lowest Concentration Point (ppm or %)	Highest Concentration Point (ppm or %)	Autologic AutoGas Analyzer
Carbon Monoxide	2.14	99.6	5000	
Carbon Monoxide (%)	0.01	3.19	7.99	0-15
Nitric Oxide	1.20	279	2795	0-5,000 (as NO_x)
Nitrogen Dioxide	0.46	358	488	
Ammonia	0.32	12.73	2995	
Sulfur Dioxide	0.98	19.6	964.5	
Ethane	1.89	100.4	1004	0-2,000 (as HC, propane surrogate)
Octane	1.12	20	1000	
IsoOctane	1.01	20	1000	
1,2,4-Trimethylbenzene	4.16	20	1000	
1,3,5-Trimethylbenzene	1.89	100	1000	
Ethylene	0.97	9.74	3000	
Propylene	4.80	89.8	194	
1,2-Propadiene	1.30	306	1020	
2-Methylpropene	1.68	150	500	
2-Methyl-2-Butene	10.26	19.57	19.57	
Ethanol	3.14	20	1000	
Methanol	1.23	18.63	931.74	
Acetylene	1.43	101.6	1016	
Propyne	4.38	50	500	
Formaldehyde	1.07	4.2	69	
1,3-Butadiene	3.09	8.3	83.4	
Toluene	15.82	18.63	931.74	
m-Xylene	5.62	93.17	931.74	
Carbon Dioxide (%)	0.08	4.6	23	0-20
Methane	1.10	414	3143	
Nitrous Oxide	0.30	146.9	200.1	
Water (%)	0.11	17.87	20.57	

Summary of Cold Start Sampling Phases

A total of six events were considered for the gas-phase exhaust species analysis as indicated in TABLE 3. Three warm-up driving events were characterized by engine cold start followed by driving under stop sign and signal controlled conditions typical of urban arterial driving. Three other events consisted of a cold start engine ignition followed by a period of extended idle, during which time the car was allowed to run and remained in park for varying lengths of time between about 900 to 3000 seconds. Each of the sampling periods included engine ignition following greater than 12 hours of cold soak. This allowed all engine components and lubricants to reach the ambient temperatures. Temperature data from the Onset HOBO logger monitoring ambient conditions was

averaged over the period from engine ignition to end of warm-up driving or extended idle for each sampling event, as tabulated in TABLE 3.

TABLE 3 Cold Start Sampling Data Collected

Event No.	Date	Ambient Temperature (°C)	Relative Humidity (%)	Phase of Sampling		
				Cold Start	Extended Idle	Warm-Up Driving
1	1-Apr-09	9.5	50.1	X	X	
2	17-May-09	20.3	25.9	X		X
3	21-May-09	38.4	19.2	X		X
4	22-May-09	24.6	39.0	X		X
5	24-Jun-09	32.4	41.3	X	X	
6	25-Jun-09	37.5	32.6	X	X	

During extended idle conditions, the vehicle was running, but the transmission remained in park. For warm-up driving, the engine was started and driving commenced after a short idle period of about a minute. The warm-up driving route was a short 0.8 mile section of a larger 35-mile test route to be used in future studies. Warm-up driving for this analysis included departure from the University of Vermont Transportation Air Quality (TAQ) laboratory and travel to the single gas station used for all gasoline refills for the study. Two traffic lights, three stop signs, and a steep downhill section provided varied conditions along the trip to the gas station. Typical operation during warm-up driving and the associated emission pattern were compared to a typical extended idle trend in FIGURE 1, illustrated by the example of ethane.

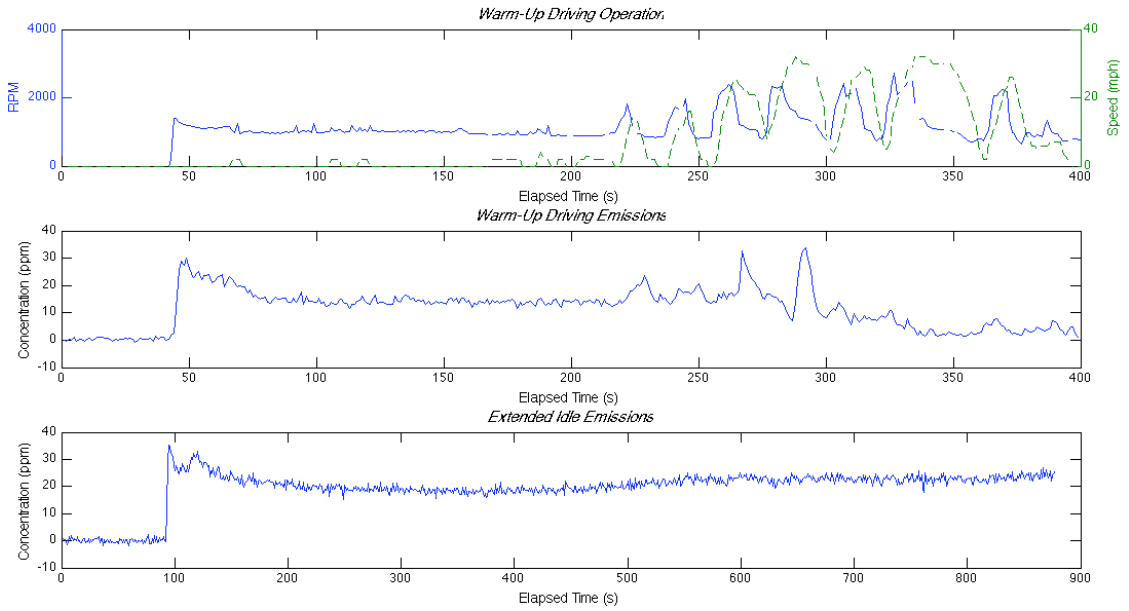

FIGURE 1 Operation parameters for warm-up driving, corresponding emissions profile for warm-up driving, and typical extended idle emissions (ethane shown as example).

In addition to the compounds explicitly measured, a summation of a selection of hydrocarbons provided a surrogate for non-methane hydrocarbons (NMHC). Typically, a single hydrocarbon or the summations of a few hydrocarbons are quantified, but in this

case the surrogate development from the hydrocarbon speciation was made based on variation in compound structure. Of the compounds selected, three have single-bonded carbons and three contain double-bonded carbons. In addition, the number of carbons varies for each of compounds, incorporating the range of hydrocarbon structures. The hydrocarbon parameter (HC*) was developed to show the relative concentration of non-methane hydrocarbons to other emissions and the relationship of HC* to ambient cold start temperatures. The value for HC* was calculated as follows:

[HC*] = [Ethane]+[Octane]+[IsoOctane]+[2-Methyl-2-Butene]+[2-Methylpropene]+[Ethylene]

where the brackets indicate the gas species concentration measured by the MultiGas in ppm.

RESULTS

Peak Cold Start Emissions

For cold starts, peak gas concentrations were examined for all species to evaluate the relative abundance of each pollutant during the warming up of the vehicle over extended idle or driving conditions following ignition (see FIGURE 2). The range of peak emissions were compared to hot-stabilized emissions from sampling on-road following a full, 2.4 mile warm-up driving schedule, indicated by blue stars in FIGURE 2. Of all of the species measured, carbon monoxide (CO) had the highest concentrations during cold start, with the maximum detected concentration during Run 1-EI (where –EI indicates 'extended idle' after cold start) at over 83,000 ppm and minimum peak emissions observed in sampling Run 4-WD (where –WD indicates warm-up driving commenced immediately after cold start) at approximately 26,000 ppm. Even this lower bound of CO peak concentration was over two orders of magnitude higher than peak concentrations measured for most other compounds. For CO, this peak occurred almost instantaneously following the engine ignition. Nitric oxide (NO) was also prevalent, as to be expected, as the significant component of the criteria pollutant oxides of nitrogen (NO_x). The peak emissions for NO did not occur immediately, but instead were elevated during the driving cycle. Other significant peak emissions included acetylene, methane, ethanol, ethylene, isooctane, octane, propylene, and toluene. Water was quantified as part of the emissions composition, producing approximately 12% stabilized water emissions on average, with the exception of the first event. The first event, Run 1-EI, with significantly colder ambient temperatures, stabilized water concentrations at about 5%.

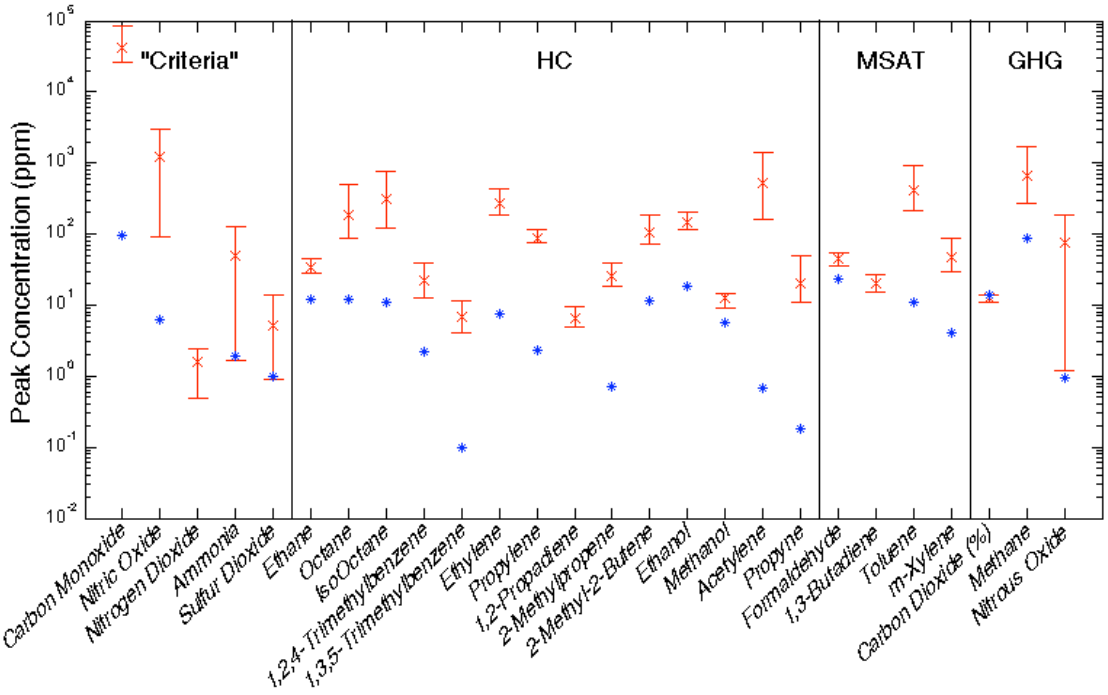

FIGURE 2 Maximum emissions concentration range (red cross and range bars) measured over six cold starts compared to typical stabilized idle emissions (blue star). The cross indicates mean of the maximum emissions, with the range bars equivalent to the maximum and the minimum peak emissions for all six events. Missing blue stars for select compounds indicate zero emissions for stabilized conditions.

Cold Start Emissions for Criteria Pollutants and Greenhouse Gases

Of the 27 gases measured, the temporal trend in concentration of two predominant emissions species, CO and CO_2, were assumed to indicate the relative operating efficiency of the vehicle's catalytic converter over time. As shown in FIGURE 3, immediately after engine start, carbon monoxide concentrations increased rapidly to the peak concentration and then decreased back to baseline levels, on average, within 90 seconds of engine start. The cold-start peak CO emissions are typically associated with low air-to-fuel ratio, or fuel-enriched conditions, as well as a cold catalytic converter. Relatively quick warm-up of the catalytic converter under the test conditions, and its increasing ability to oxidize CO to CO_2 as time elapsed from ignition, is indicated by the increase in CO_2 that occurred after the time of CO peak emissions. The time to optimal efficiency of emissions control devices varied tremendously for other emissions species, specifically NO_x and MSATs.

For the warm-up driving cold start tests, (Runs 2-WD, 3-WD, and 4-WD in the right hand panel of FIGURE 3) the end of the sampling period was indicated by engine off for refueling at the gas station, resulting in a drop in CO_2. The three cold starts without driving cycles (Runs 1-EI, 5-EI, and 6-EI) produced steady CO and CO_2 emissions over the extended idle period.

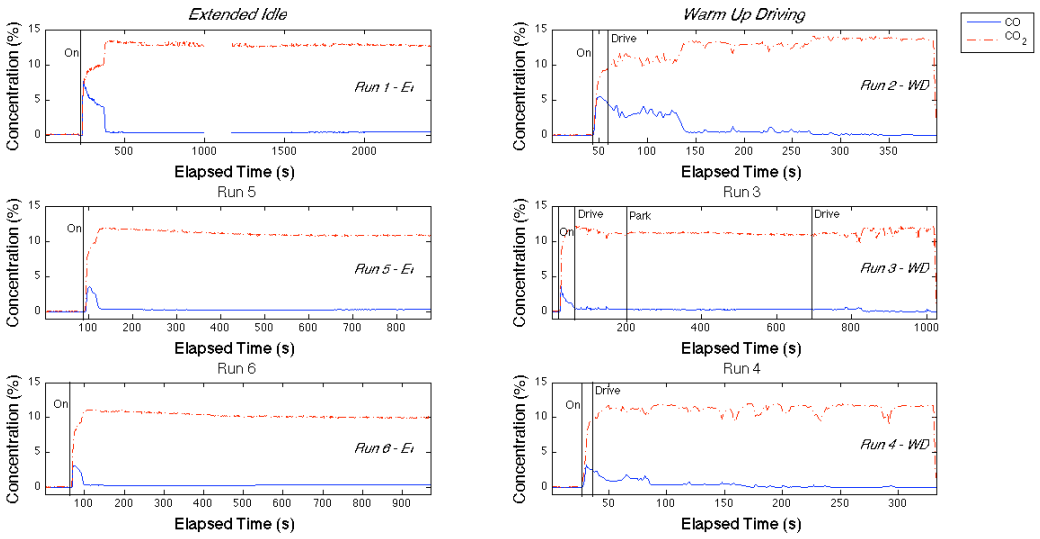

FIGURE 3 Second-by-second CO and CO_2 emissions during cold start runs. Plots on left for cold starts with extended idle. Plots on right are for cold starts with warm-up driving.

Nitrogen species emissions patterns were somewhat different from CO (see FIGURE 4). Nitric oxide was emitted at an average of approximately 100 ppm with the initial cold start of the engine. Beyond the initial peak emission, NO concentrations depended on vehicle operation. During extended idle tests (left panels, FIGURE 4) the vehicle continued to emit relatively stable concentrations of NO and concentrations gradually increased at idle conditions beyond about 300 seconds after ignition. As soon as the vehicle was put into gear for driving, the NO concentrations increased (right panels, FIGURE 4), sometimes to concentrations that exceeded the ignition peak. These higher NO concentration peaks were likely a result of engine loading. It was not until driving was continued for 100 to 200 seconds that the concentration peaks diminished significantly and other nitrogen species were present at low concentrations. The vehicle was not able to convert the NO pollutant to other, less harmful compounds until close to the end of the warm-up driving. It is important to note that for Run 3-WD, the NO concentration pattern clearly depicts the initial shift into drive (indicated by the Drive partition in FIGURE 4), the shift into park about 150 seconds later (indicated by the Park partition), and the short period of idling that occurred while a GPS error was fixed.

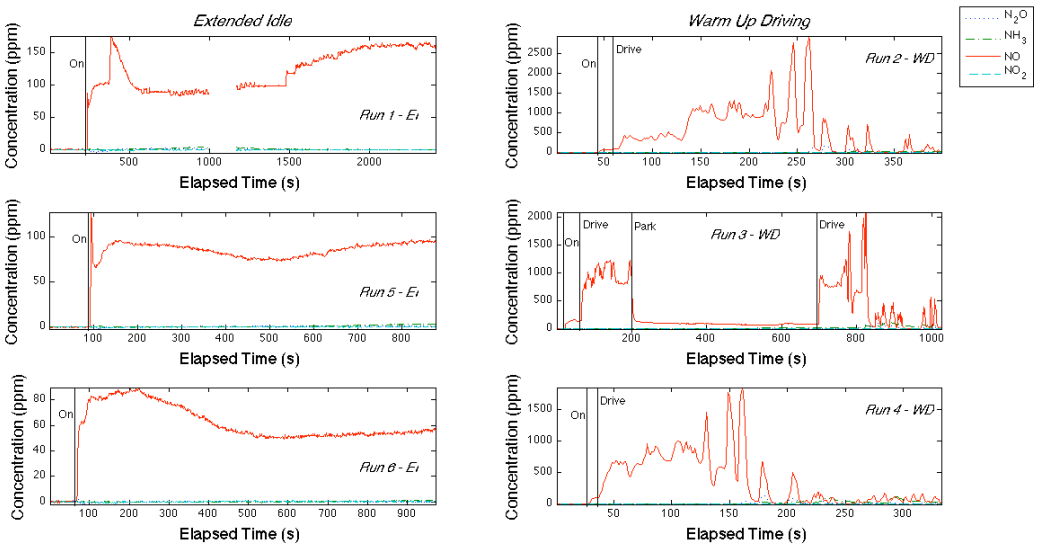

FIGURE 4 Nitrogen species over the course of extended idle and warm-up driving cold starts.

Air Toxic Cold Start Emissions

In general, air toxic species (defined here as formaldehyde, 1,3-butadiene, toluene and xylenes) increased sharply at engine ignition. Of the MSAT species quantified, formaldehyde behaved unlike the other species. The peak formaldehyde emissions during cold start were approximately 45 parts per million. When driving commenced, indicated by Drive partitions in sampling Runs 2-WD, 3-WD, and 4-WD (right panels, FIGURE 5), the formaldehyde concentrations increased further to the peak emissions levels, and then decreased gradually to near baseline levels within 100 to 200 seconds of driving (Drive partitions). During the extended idle conditions encountered in sampling Runs 1-EI, 5-EI, and 6-EI (left panels, FIGURE 5), formaldehyde concentrations did not decrease back to baseline levels, but continued to increase slightly during the entire cold start and idle sampling period. The pattern of formaldehyde emissions indicates that the extended idle conditions were not sufficiently warming up the catalyst that would typically diminish formaldehyde emissions. In contrast, stop-and-go driving resulted in baseline formaldehyde concentrations within approximately 200 seconds of the Drive partition, indicating the driving start. The MSAT compound 1,3-butadiene behaved similarly to formaldehyde in that it reached its peak emissions point either through gradual increase over extended idle, or by reaching a plateau at high concentrations during the course of stop-and-go driving. Unlike formaldehyde, however, the decrease from peak 1,3-butadiene emissions was not gradual, but nearly instantaneous, apparently at the point of catalyst optimization (but different from the optimization point as determined from CO/CO_2 relationships).

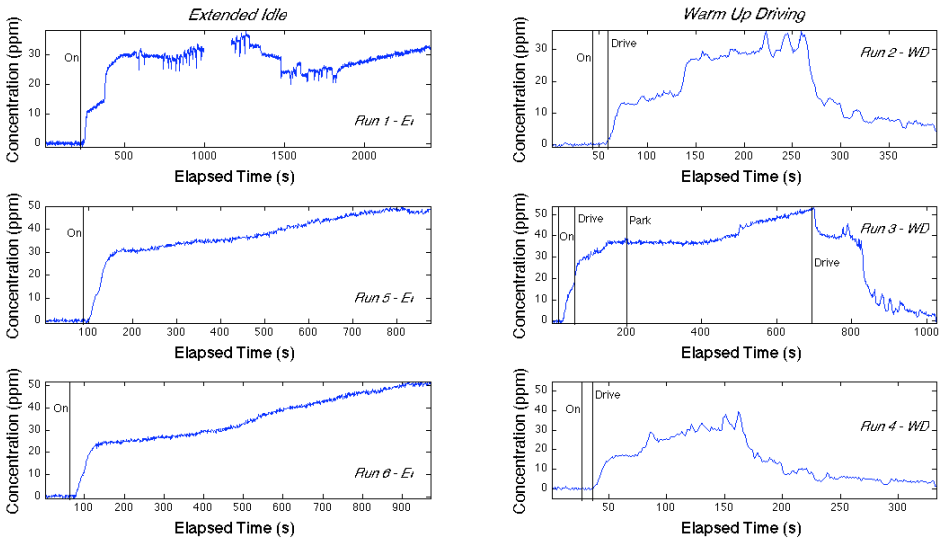

FIGURE 5 Formaldehyde emissions trends over cold start sampling.

Similar to formaldehyde, other MSAT emissions species concentrations increased sharply at engine ignition, but, unlike formaldehyde, toluene and m-xylene reached their maximum emissions point nearly instantaneously. For toluene (FIGURE 6) and m-xylene (data not shown), the maximum peak emissions were recorded within five seconds of engine ignition, similar to the initial startup behavior exhibited by CO. Extended idle conditions resulted in stabilized toluene concentration plateaus at levels less than the initial peak concentration (FIGURE 6, left panel). The concentration plateaus increased slightly after about 400 seconds of extended idle for Run 5-EI and Run 6-EI. Switching the vehicle to driving conditions again resulted in decreasing concentrations for these MSATs over time, best illustrated by the trends from Runs 2-WD and 4-WD in FIGURE 6. M-xylene time-series trends were similar to those for toluene, just at a lower concentration. It is important to note that the idling period that occurred after the vehicle was put into gear in Run 3-WD of FIGURE 6 (indicated by the time between the Park partition and the second Drive partition), resulted in a gradual increase to a plateau concentration of about 150 ppm. Thus, while the vehicle was in park for Run 3-WD, the trend of emissions concentrations reproduced the extended idle trend in Run 5-WD and 6-WD (left panels, FIGURE 6). Once the vehicle was switched into gear again and driven, the emissions pattern changed to the warm-up driving trend of decreased concentrations with drive time that was presented for Run 2-WD and 4-WD (right panels, FIGURE 6).

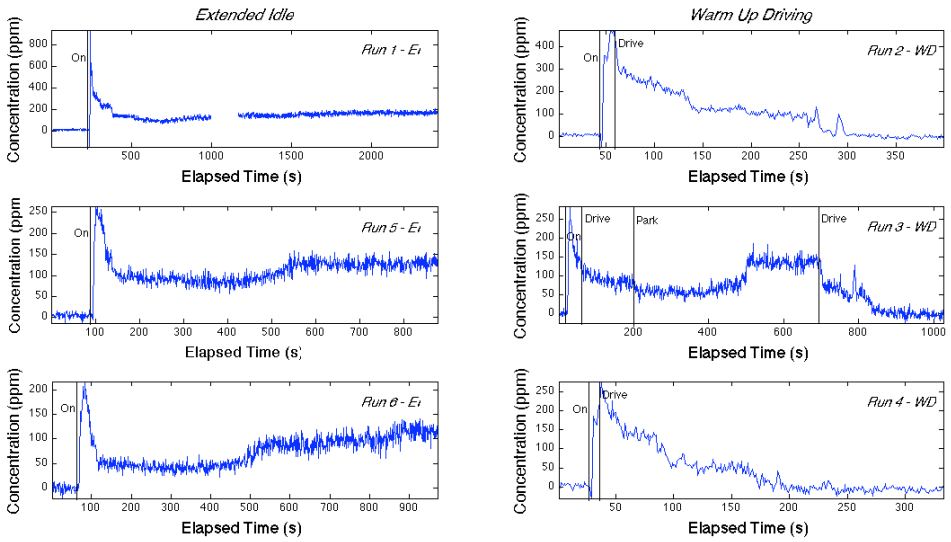

FIGURE 6 Toluene cold-start emissions trends.

The four MSAT species investigated showed two distinct time trends. Toluene and m-xylene would be expected components of gasoline, and the excess unburned fuel at initial ignition would correspond to the peak emissions of those species. Formaldehyde and 1,3-butadiene are products, or even secondary products, of the combustion process, indicated by the oxygen-containing structure and the structure with two double bonds, respectively. The two distinct responses of these compounds after cold start of the engine results from two of the compounds being components of fuel and two being by-products of combustion. The initial elevated emissions for toluene and m-xylene, along with the eventual peak emissions from formaldehyde and 1,3-butadiene were produced at concentrations well above the detection limits for the instrument. Toluene peak emissions reached the upper calibration concentration limit of 932 ppm, previously reported in TABLE 2, during the first sampling event. Formaldehyde peak emissions were in the upper range of the quantitation limits, but did not exceed the upper limit. Hot-stabilized emissions were well below peak emissions for these four compounds, the closest being formaldehyde with hot-stabilized emissions ranging 1.5 to 2 times below the peak emissions from the six sampling events.

Ambient Temperature Effects on Cold Start Emissions

It is well documented that temperature influences cold start emissions and this relationship is generally attributed to the requirement of establishing enriched air-to-fuel conditions at colder ambient temperatures for engine ignition, as previously discussed.

Species from each category of emissions ("criteria" pollutants, hydrocarbons*, greenhouse gases, and MSATs) were plotted to show the general relationship of temperature to peak concentration in FIGURE 7. Over the six runs, an inverse relationship of peak gas concentrations as a function of cold start mean temperature was established for many of the compounds, with the exception of CO_2 (FIGURE 7). Only at the hottest average temperature experienced in the sampling (38.4°C, Run 3-WD) did that trend change for the compounds examined.

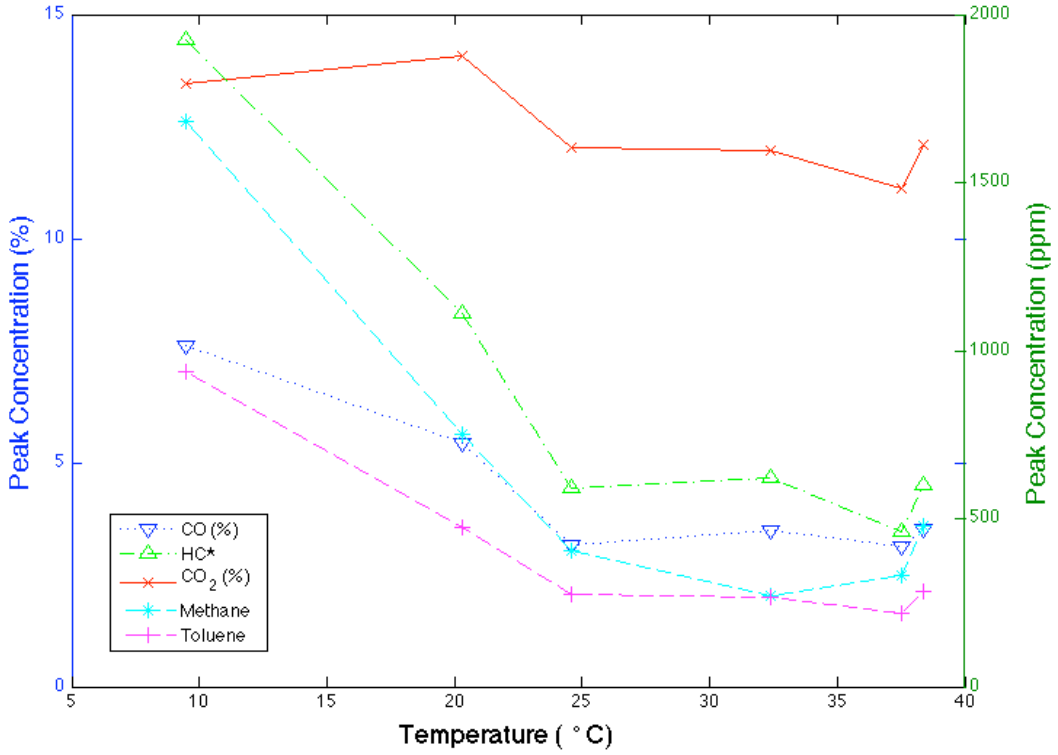

FIGURE 7 Peak emissions at cold start as a function of average ambient air temperature for six sampling events.

CONCLUSIONS

The gas-phase emissions during cold start of the 1999 Toyota Sienna minivan indicate that optimal function of the emission control devices can not be based solely on conversion of pollutants (i.e., CO) to less harmful by-products of combustion (i.e., CO_2), because the time frame associated with individual pollutant conversion varies by species. For some criteria pollutants, like nitric oxide, warm-up driving operation produced elevated emissions induced by loading the engine. Carbon monoxide, another criteria pollutant, was emitted at high concentrations during enriched engine ignition conditions, but was mitigated relatively quickly as the catalyst achieved optimum operating conditions. Additionally, driver behavior after initial engine cold start was found to have a significant effect on gas-phase emissions, including the air toxics examined in this study. The air toxics were found to persist in high concentrations with extended idle conditions, as compared to the lower concentrations associated with warm-up-driving. The magnitude of the concentration changes between these driving behaviors varied between compounds.

Overall, conversion of carbon monoxide to carbon dioxide emissions was examined to define the cold start and time to optimal oxidation of the pollutant. This time frame, however, could not be used as an indicator for optimal emission control device operation (and the end of "cold start" emissions behavior), as it did not necessarily correspond to

the pattern observed for other components of exhaust that were apparently affected differently by the catalyst. The behavior trend of CO and CO_2, under 9.5°C to 38.4°C ambient temperature test conditions, took approximately 90 seconds, on average, to convert the pollutant almost entirely to the greenhouse gas, indicated by the sharp decrease in CO and increase in CO_2. The characteristic CO and CO_2 trends were demonstrated regardless of the driving cycle or idle condition following the cold start of the engine. This might be expected as catalytic converters were first designed to control CO emissions.

The MSATs, in contrast, were more sensitive to the driving versus idle condition. With extended idle, formaldehyde and 1,3-butadiene continued to increase during the entire sampling periods, ranging from 900 to 3000 seconds. Toluene and m-xylene reached peak emissions within seconds of engine ignition for all sampling events, but after stabilized, lower concentrations were established, they also trended positively as extended idle continued. For warm-up driving, 1,3-butadiene and formaldehyde reached peak emissions during the course of driving, but all of the MSATs examined decreased significantly within 100 to 200 seconds of driving. The preliminary results of this study suggest recent efforts to reduced vehicle idling behavior may have implications beyond the fuel and emissions savings. Reduction in idling time could mitigate the elevated concentrations achieved in this study for extended idle conditions, as compared to the warm-up driving scenarios. With particular consideration of the health effects associated with MSAT emissions, these results suggest that periods of extended idling after cold starts prolong potential exposure at elevated concentrations of these toxic species. Furthermore, the MSATs data indicate that minimizing idle times will have significant air quality and human health benefits. Limiting idle to the approximate time it takes for the initial peak of fuel constituents, as little as a minute, could prevent further exposure to the air toxics.

Ambient temperature affected CO, HC*, methane, and toluene peak emissions significantly, illustrating decreasing peak concentrations for compounds from each previously defined emission category (“criteria”, hydrocarbons, MSATs, and greenhouse gases) as temperature increased over the range from 9.5°C to 38.4°C. Only at the highest temperature were these species not subject to the inverse trend. CO_2 did not respond to temperature changes over the course of the sampling events to the same extent as the other compounds investigated, but instead stabilized at approximately the same range of concentrations from 11% to 14%. The advantage of TOTEMS is that the cold start sampling - idling - driving tests were performed in real-world scenarios, testing the temperature trend in actual vehicle application. Future work with TOTEMS, sampling over seasonal conditions, will further investigate the relationship of real-world temperature, including sub-zero winter temperature, influences on vehicle emissions.

Overall understanding of MSAT trends helps to inform models to better predict these toxic emissions for purposes of environmental air quality and human health and exposure. Peak MSAT emissions during cold start events were found to respond to temperature similarly to HC*, CO, and methane, making these species possible predictors of MSAT emissions under various temperatures, for modeling purposes. In addition, the

increasing concentration behavior of MSATs under extended idle conditions, unlike the decreasing emissions observed for immediate driving, may be an area to investigate in terms of human health exposure to these toxic emissions.

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