Time Resolved Measurements of Speciated Tailpipe Emissions from Motor Vehicles: Trends with Emission Control Technology, Cold Start Effects, and Speciation

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⑤ *Supporting Information*

ABSTRACT: Experiments were conducted at the California Air Resources Board Haagen-Smit Laboratory to understand changes in vehicle emissions in response to stricter emissions standards over the past 25 years. Measurements included a wide range of volatile organic compounds (VOCs) for a wide range of spark ignition gasoline vehicles meeting varying levels of emissions standards, including all certifications from Tier 0 up to Partial Zero Emission Vehicle. Standard gas chromatography (GC) and high performance liquid chromatography (HLPC) analyses were employed for drive-cycle phase emissions. A proton-transfer-reaction mass spectrometer measured time-resolved emissions for a wide range of VOCs. Cold-start emissions occur almost entirely in the first 30−60 s for newer vehicles. Cold-start emissions have compositions that are not significantly different across all vehicles tested and are markedly different from neat fuel. Hot-stabilized emissions have varying importance depending on species and may require a driving distance of 200 miles to equal the emissions from a single cold start. Average commute distances in the U.S. suggest the majority of in-use vehicles have emissions dominated by cold starts. The distribution of vehicle ages in the U.S. suggests that within several years only a few percent of vehicles will have significant driving emissions compared to cold-start emissions.
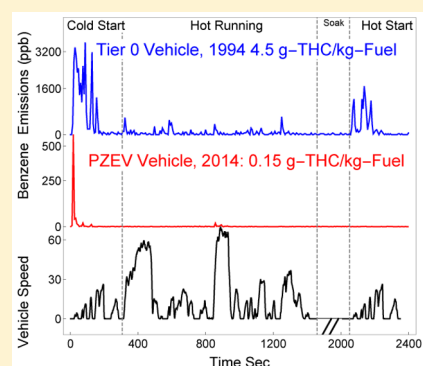
1. INTRODUCTION

U.S. emissions standards for vehicles have decreased by over a factor of 20 in the past 20 years.[1] To meet these standards, engine and emissions control technologies have advanced to decrease both the magnitude of driving emissions and duration of cold start emissions of hydrocarbons and criteria pollutants. Reduction of vehicle emissions, particularly nonmethane organic gases (NMOG), will continue to be a major focus for improving air quality in the U.S. Major innovations to reduce vehicle emissions have been improved measurement and control systems as well as improved sensors components and actuators. Advances in these three areas continue to be the important routes to lowering vehicle emissions, and a major outcome has been to further compress emissions to distinct events during vehicle operation (e.g., engine start and hard acceleration). Correlating emissions and engine activity thus requires characterization of emissions with increasingly higher time resolution. In addition, the complex nature of secondary pollutant formation, such as ozone and secondary organic aerosol (SOA), requires detailed speciation of a wide range of NMOG compounds.

Controlled vehicle testing clearly shows that cold starts dominate emissions, because the catalyst is not fully active, allowing unburned and incompletely combusted material to pass through exhaust after-treatment systems[2,3] The ratio of total emissions from cold start to per-mile hot-stabilized emissions (γ) can be used as a metric of the relative impact of cold start emissions.[4] Values of γ for NMOG may reach hundreds of miles, meaning that emissions are dominated by cold starts for any distance shorter than this. Cool-starts, which occur when the engine is somewhere between ambient and hot-stabilized temperature are also common. Cool-start emissions may reach 20% of cold start emissions after a soak-time (time between a cold-start and the next engine start) of just 1 h.[5] While this is true for properly operating vehicles, on-road tests suggest during hot-stabilized operation emissions are dominated from a limited number of high emitting vehicles with catastrophic failure of their emissions controls.[6−10]

Health impacts of vehicle emissions are strongly tied to emissions composition. Toxicity of emissions and their contribution to secondary pollutants (e.g., ozone and PM$_{2.5}$)

depend on the particular species that are emitted, such as the BTEX (benzene, toluene, and xylenes) compounds and oxygenated species such as acetaldehyde. Due to the difficulty in sampling actual vehicle exhaust, fuel composition may be used to approximate exhaust composition. This approach is useful for fuel-based estimates of emissions and laboratory experiments on secondary pollutant formation, allowing the use of a readily available precursor mixture, but exhaust composition can differ from fuel composition and varies with driving conditions[11−13] Detailed composition measurements of actual exhaust are thus required and must continually be updated as new emissions controls systems are implemented to meet new emissions standards.

To address the issues stated above, rapid and comprehensive measurements of speciated NMOG emissions are needed, especially as cold-start emissions continue to shorten. Currently 1 Hz measurements have been made for gas species including the BTEX compounds, small carbonyls, acids, and some nitrogen containing compounds using FTIR and/or chemical ionization mass spectrometry (CIMS), but high time resolution studies of vehicle emissions are limited and not routine.[14−21] While routine real-time measurements include CO_2, CO, and HC; here we focus on high-time resolution of a range of individual NMOG species to give broader insight into the changing effects of new emissions control technologies and project future vehicle fleet emissions, both in terms of species profiles and identifying future needs in emissions controls. This paper presents measurements of a wide range of individual NMOGs in tailpipe emissions during chassis dynamometer testing of gasoline vehicles recruited from the Southern California fleet to determine the effects of control technologies on both emissions time-profiles and their speciation.

2. EXPERIMENTAL METHODS

2.1. Fleet Overview. The test fleet included 20 light duty gasoline vehicles recruited from southern California rental agencies, the ARB vehicle pool, and southern California residents. The vehicles spanned model years from 1990 to 2014 and therefore featured a range of engine and emission control technologies. The vehicle fleet was chosen to examine the effectiveness of the newest emissions control systems with enough older vehicles to provide context and continuity with previous studies. For discussion, the gasoline vehicles are classified by their emissions certification standard. The test fleet included one Tier 0 vehicle (T0), one low emission vehicle (LEV I), two tier two low emission vehicles (LEV II) vehicles, five ultralow emission vehicles (ULEV), five superultra-low emission vehicles (SULEV), and six partial-zero emission vehicles (PZEV). A complete list of vehicles is provided in the Supporting Information (SI).

2.2. Dynamometer Tests. All vehicles were tested on a chassis dynamometer using the standard Unified Cycle (UC) driving protocol at the California Air Resources Board (ARB) Haagen-Smit Laboratory. The UC driving protocol consists of three operating phases: cold-start, hot-stabilized, and hot-start. The UC protocol is similar in overall duration and distance to the Federal Test Procedure (FTP), but it was developed specifically to represent driving in Southern California. It has aggressive driving with harder acceleration periods than the FTP, which results in higher emissions.[22] The FTP protocol is used to certify emissions standards for both the ARB and US EPA, though the same trends in emissions due to changes in vehicle technology are expected for either drive protocol. The

UC has been used for emission inventory development. Recent work has used the UC protocol, allowing for more direct comparison in trends of emissions across studies and test fleets.[1,2,23−26] Prior to cold-start tests vehicles were conditioned with an overnight soak. Tailpipe emissions were sampled directly into a constant volume sampler (CVS) that diluted the exhaust by a factor of 10−30. Vehicles used a commercial summertime gasoline provided by ARB; composition analysis completed by ARB is provided in SI.

2.3. Real Time Measurements. Diluted exhaust was sampled from the CVS into the proton transfer reaction mass spectrometer (PTR-MS) using a heated $^1/_2$ in. diameter transfer line made of passivated stainless steel followed by an unheated, $^1/_8$ in. diameter passivated steel tube. Prior to the PTR-MS the emissions were further diluted by a factor of 10−100 using filtered air. This second stage of dilution was required to ensure that the reagent H_3O^+ ions were not significantly depleted in the PTR-MS. The PTR-MS measured gas-phase compounds with a quadrupole mass analyzer (Ionicon Analytik). A 6 s scan was used to cover all masses from 21 to 140. Monitoring the signal for water clusters (i.e., humidity) showed that the instrument responded faithfully to engine activity, as water is always produced from combustion.

The PTR-MS was calibrated using a custom mix of standard gases (Scott-Marin Gases) and a custom built calibration unit with a platinum catalyst to provide VOC-free air for accurate dilution of the standard. Measurements during drive cycles were background subtracted and quantified. The PTR-MS data generally agreed to within 30−40% of standard GC/LC measurements by ARB, described below (Figure S1). Due to sample analysis considerations, the data set for the PTR-MS, which is obtained in real-time, included more experiments (48) than the GC-FID measurements (13).

2.4. Bag Integrated Measurements. Dilute exhaust was sampled into Tedlar bags for measurements of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4)), and total hydrocarbons (THC) by drive cycle phase; analysis for these species was completed shortly after each drive test. Bag 1, bag 2, and bag 3 correspond to the cold-start, hot-stabilized, and hot-start drive cycle phases, respectively. Analysis of total exhaust gases was performed using an AMA-4000 measurement system (AVL North America, Inc., Plymouth, MI). Total hydrocarbons were measured with Flame ionization detection (FID) that was calibrated daily using a methane/propane blend.[27] Methane was measured by gas chromatography-FID, and CO and CO_2 by nondispersive Infrared (NDIR) detectors (IRD-4000). Individually speciated organic gases were measured using GC-FID.[28] Carbonyl emissions were measured from samples collected on 1,4-dinitrophenylhydrazine (DNPH) impregnated cartridges (Sep-Pak DNPH-Silica Cartidges Plus-Long Body, Waters Corporation, Milford, MA) analyzed by high-performance liquid chromatography.[29]

2.5. Emission Factors. Emissions are presented using emission factors, as mass emitted per mass of fuel consumed, using a mass balance approach:

$$EF_i = \Delta m_i \frac{x_c}{\Delta CO_2 + \Delta CO + \Delta THC} \qquad (1)$$

ΔCO_2, ΔCO, and ΔTHC are the background-corrected concentrations of CO_2, CO, and THC. The fuel had a carbon mass fraction, x_c of 0.82. Δm_i is the measured background corrected concentration of species i. Measured fuel con-

sumption per mile for each test is provided in the Supporting Information for conversion to distance-based emission factors.

3. RESULTS AND DISCUSSION

3.1. Overall Fleet Emissions. *3.1.1. Total Hydrocarbons.*
As expected, the total hydrocarbon (THC) emissions for the full UC drive protocol have decreased significantly in accordance with stricter vehicle emissions standards. The results for our fleet augmented by previous measurements[2] are shown in Figure 1 as box-and-whisker plots. Note the
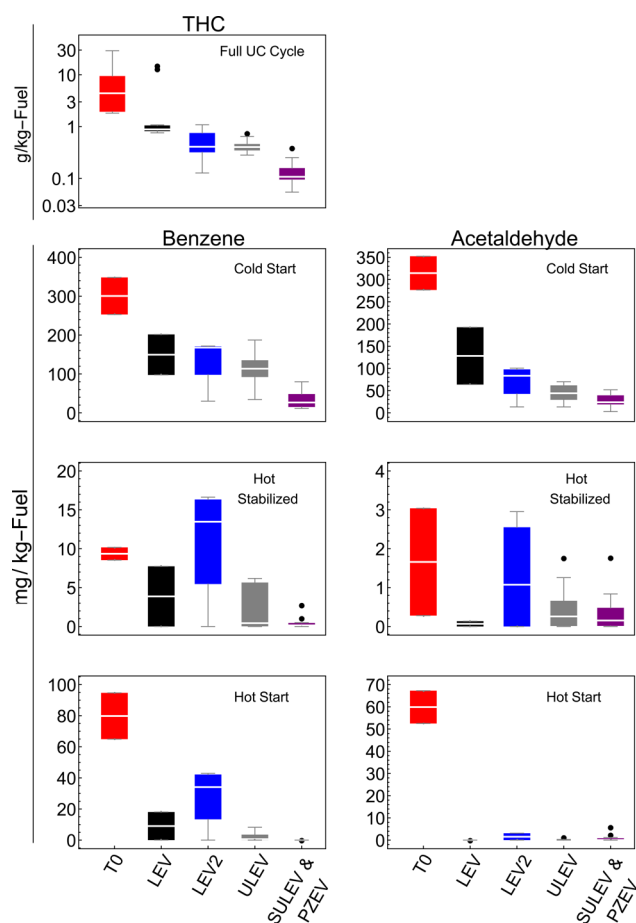

Figure 1. Total hydrocarbon emissions for the complete UC drive protocol. Includes data for Tier 0, Tier I, and Tier II vehicles from a previous study,[13] (top panels). Benzene (lower left) and acetonitrile (lower right) emission factors for each phase of the UC protocol for all vehicle classes as measured by PTR-MS for the current study only. The central white lines on the box plots are median values; the edges of the boxes are the 25th and 75th percentiles; the whiskers extend to the most extreme data not considered outliers; black points are determined to be outliers.

logarithmic scale. The number of vehicles included is 8 for the combined SULEV and PZEV vehicles, the other classes include 11 or 12 vehicles. From Tier 0 (pre-LEV) to SULEV and PZEV vehicles, the decreases in median THC emissions are a factor of 40.

3.1.2. BTEX Compounds. Benzene emissions as measured by PTR-MS for our test fleet show strong reductions for vehicles with newer emissions controls. This data is shown in the lower left section of Figure 1 for the UC drive protocol. There is a clear decreasing trend for cold-start (bag 1) emissions, which includes the first 300 s after engine start. SI Figure S2 shows

this data for all BTEX compounds. The oldest Tier 0 vehicle has emissions that are between 13 (benzene) to 20 (toluene and xylenes) higher than the PZEV vehicles that meet much stricter emissions standards. While the current study has only a single Tier 0 vehicle, this vehicle had emissions similar to other Tier 0 vehicles in a previous study with a larger number of vehicles.[13] Both control system technology and its condition contribute to these decreases in emissions. For hot-stabilized operations (bag 2), there is much less of a trend with vehicle technology/condition, and most of the emissions in bag 2 are associated with hard accelerations. Hot-start (bag 3) emissions are again highest for the Tier 0 vehicle. The high hot-start emissions for one of the LEVII vehicles strongly suggest emissions controls that are in poor condition. This is also supported by the fact that this part of the drive cycle does not have hard accelerations. Looking across technologies we see that even the LEV I vehicle (certified to a less strict standard) has lower emissions than this LEV II vehicle in both bags 2 and 3. These observations suggest that the bag 3 emissions from the LEV II vehicle are most likely due to a poorly functioning catalyst. Vehicles in the PZEV and SULEV class show slight emissions during bag 2, indicating that hard acceleration and high fuel delivery can overwhelm even new technology catalysts when they are hot. They show extremely low emissions during hot-start. The Tier 0 and LEV II vehicle with high emissions will be discussed in further detail below, as indicators of how the future vehicle fleet will be affected by aging vehicles with poorly functioning emissions controls.

3.1.3. Differences in BTEX Composition Between Exhaust and Fuel. The relationship between the unburned gasoline and tailpipe exhaust composition can be important for modeling emissions, secondary pollutant formation, and source apportionment. A metric for the similarity between exhaust and fuel, particularly for predicting formation of SOA, is the fraction of total BTEX from its three constituents: benzene, toluene, and the xylenes. Figure 2 shows that exhaust from all vehicle classes
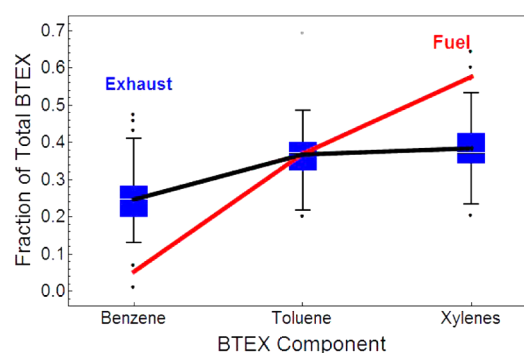
Figure 2. BTEX composition for exhaust from gasoline vehicles in this study and an earlier study,[2] both performed at the ARB Hagen-Smit Laboratory with the UC drive protocol. The xylenes category includes ethylbenzene. Exhaust data includes vehicles from all classes with number of vehicles in parentheses. (T0(15), LEV I(20), LEV II(27), ULEV(5), SULEV(6), PZEV(6)).

spanning over 20 model years have a similar BTEX composition, including data from previous work.[2] Compared to the fuel composition, the exhaust has distinctly higher proportions of benzene and lower proportions of xylenes compared to unburned fuel. For benzene, toluene, and xylenes, the average fractions by vehicle class are within the range (0.21−0.27), (0.33−0.4), and (0.37−0.41). No trend in the

exhaust BTEX composition was observed moving from older to newer technologies. For the purposes of converting fuel usage data to actual emissions data, we recommend that the BTEX composition in the fuel can be multiplied by factors of 5, 1, and 0.6 for benzene, toluene, and (xylenes + ethylbenzene) to approximate the BTEX composition of emissions. This increase in benzene, known to result from catalytic converter effects, and these multipliers are similar to previous results for gasoline vehicles.[13,30,31] The BTEX compounds are important SOA precursors and air toxics, so accurate representation of this class of compounds is important in atmospheric modeling of SOA and human exposure. It appears that emissions controls exhibit a fairly constant BTEX profile, so although the exhaust composition is different from the initial fuel, it is nonetheless fairly constant for a given fuel input.

3.1.4. Incomplete Combustion Products. Gas-phase products from incomplete combustion of fuel are emitted in addition to unburned fuel. The lower right section of Figure 1 shows results for bag-integrated PTR-MS measurements of acetaldehyde, which is readily detected using PTR-MS and not present in fuel. The trend for cold-starts is as expected; exhaust emissions drop significantly with newer control technologies. Hot-stabilized emissions are 1−2 orders of magnitude below bag 1 emissions. The Tier 0 and LEV II vehicles have the highest acetaldehyde emissions during hot stabilized operation. While ULEV and SULEV vehicles can emit as much as these older vehicles, median acetaldehyde emissions decrease with newer technologies during hot stabilized operation. During hot start, the Tier-0 and LEV II vehicle stand out with the highest bag 3 acetaldehyde emissions, whereas the other classes had hot-start acetaldehyde emissions near or below 1 mg/kg-Fuel. Notably, the outliers in the SULEV and PZEV classes are hybrid vehicles. These PTR-MS results show that cold-starts can be expected to dominate emissions of incomplete combustion products, even for poorly functioning vehicles.

Other ketone and aldehyde emissions were dominated by acetone and formaldehyde. This was true across all vehicle classes and ages. These emissions, as measured using DNPH cartridges followed by analysis by HPLC, are shown in SI Figure S3. The number of vehicles included is limited for these oxygenated species: PZEV(4), SULEV(3), ULEV(7), LEV II(2), LEV I(1), Tier-0(1). Emissions of these unsaturated ketones and aldehydes decrease dramatically for vehicles that meet newer emissions standards. Methacrolein and acrolein were detected in nearly all vehicle classes, with acrolein not detected in ULEV or PZEV vehicles (SI Figure S3). A notable exception is methacrolein during hot starts, where the LEV II vehicle has emissions as high as the Tier-0 vehicle. The PZEV vehicle that had detectable methacrolein during bag 2 was the only hybrid PZEV vehicle tested. Propionaldehyde was a minor contributor for Tier 0 to ULEV vehicles, and only for cold-starts. Other ketones and aldehydes that were monitored but had emissions near or below reporting limits included methyl−ethyl−ketone, butyraldehdye, hexanal, valeraldehyde, and crotonaldehyde.

3.1.5. Overall VOC Composition. The varying composition of exhaust by vehicle class was assessed, in part, by comparing the mass fraction of BTEX compounds in NMOG emissions. These data are shown in SI Figure S4. For cold start emissions, benzene and toluene are a similar fraction of NMOG mass across all vehicle classes, centering on a value of 0.04 mg/mg-THC. Xylenes + ethyl-benzene to THC ratios for cold-start emissions declined slightly for vehicles meeting stricter

emissions standards, with medians decreasing by about 20% between Tier-0 and LEV I vehicles and those meeting stricter standards. The upper quartile for vehicles meeting LEV II and stricter certifications was also below the median of the Tier 0 and LEV I vehicles. Hot-stabilized emissions showed some enhancement of BTEX composition for vehicles meeting stricter certifications. Hot-start emissions showed significant fractions of benzene for vehicles up to ULEV, with values between 0.01 and 0.05 mg/mg-THC, whereas SULEV and PZEV vehicles showed almost no benzene emissions. Toluene and xylenes + ethylbenzene hot-start fractions declined with stricter emissions control systems. Because cold-start emissions are dominated by unburned fuel and all vehicles used the same fuel, it is not surprising that BTEX emissions as a fraction of THC emissions do not vary significantly across control technologies. Conversion of larger alkyl benzene compounds to benzene is known to occur, and it appears that newer technologies (catalysts) behave similarly to older technologies in this respect.[31−33]

The average mass spectra observed by PTR-MS are shown in SI Figure S5 for each vehicle class studied. SI Figure S6 shows the total PTR-MS signal broken into five chemical categories: alkanes, BTEX, speciated alkenes, speciated oxygenated compounds, and compounds that have parent/fragment masses without explicit identification (unknown). The alkanes signal is mainly derived from ionization by O_2^+ and subsequent fragmentation, and the speciated compounds, including BTEX, are measured via H_3O^+ ionization.[34] The mass fragments in the unknown category have been separated into even and odd masses. Odd mass fragments, except the well-known alkane fragments, are associated with ions from H_3O^+ ionization. Even masses in the unknown category may either undergo H_3O^+ ionization and contain nitrogen or be associated with O_2^+ or NO^+ ionization.

Alkanes are generally 30−40% of total PTRMS signal; the BTEX compounds are 20−40%; and other speciated compounds are typically 20−30%. The unknown category is generally less than about 10% of the total PTR-MS signal. The majority of the unknown compounds appear at odd masses attributable to H_3O^+ ionization and their sensitivity will thus be similar to speciated oxygenated compounds. This suggests that the mass of unidentified compounds is generally less than 30% of speciated oxygenated compounds and about 15−25% of BTEX compounds. Previous studies have suggested the potential for newer vehicles to have mixes of exhaust gases that are more potent SOA precursors, per total mass of emissions, than older vehicles.[23] If vehicle exhaust composition, rather than total mass of emissions, were becoming a dominant factor for vehicle-derived SOA, future regulations would need to target specific compounds or classes of compounds. If any change in potency for SOA formation has occurred, our results do not suggest it is related to changes in VOC emissions, though variation in lower volatility emissions is possible. Our overall VOC composition measurements show similar VOC composition for all vehicle classes.

3.2. Time Resolved Resolution Measurements.
3.2.1. Nonoxygenated/Fuel-Derived Emissions. Time resolved emissions, as measured by PTR-MS, are shown in Figure 3 for benzene (m/z 79, blue), acetaldehyde (m/z 45, red), and aliphatics (m/z 57, black), normalized to their maximum signals. The drive cycle speed trace is in shown gray. Figure 3a shows emissions from the vehicle that met the least stringent emission standard (T0, 1990); 3b, a moderate-age, medium-
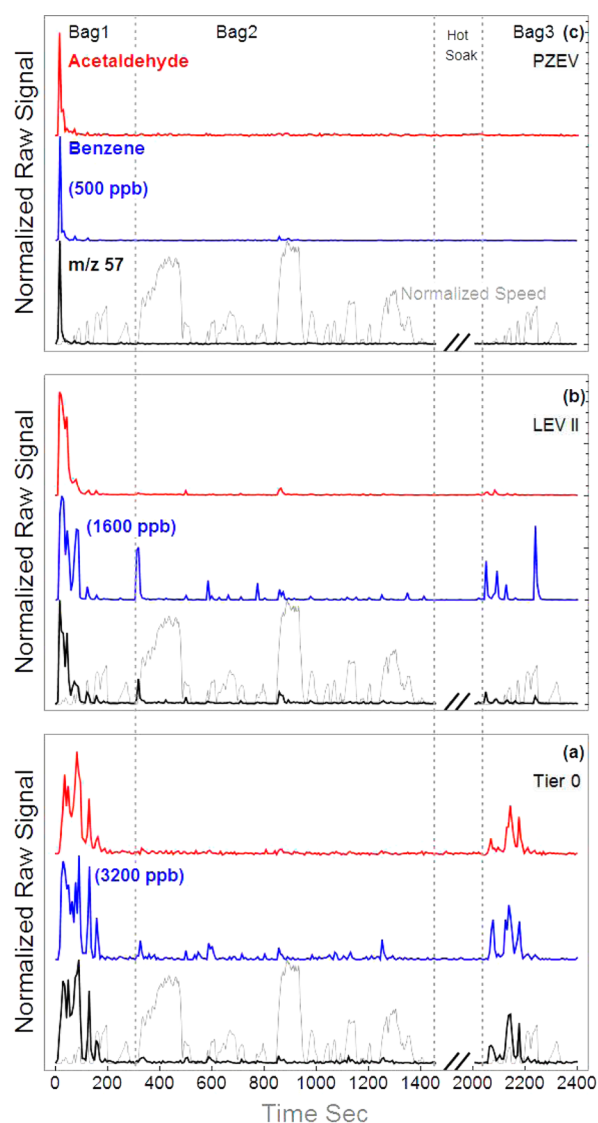
Figure 3. Time resolved PTR-MS measurements of benzene (m/z 79, blue), acetaldehyde (m/z 45, red), and aliphatic compounds (m/z 57, black) for a PZEV (c), a malfunctioning LEV II vehicle (b), and a Tier 0 vehicle (a) for the UC testing protocol. Data are normalized to peak signal for each species. Values for the peak concentrations of benzene are shown in blue. The drive trace is shown in gray, with a maximum speed of 67 mph.

emissions vehicle (LEV II, 2008); and 3c, a new vehicle that meets the strictest emissions standard (PZEV, 2013). The peak benzene concentrations in the CVS are shown in blue with the corresponding benzene signal trace. The benzene emissions data show that newer and advanced emissions control systems reduce both the peak concentration of emissions and the duration of emissions spikes throughout the drive cycle. The PTR-MS time-traces for aliphatics (m/z 57) show a similar trend.

Both benzene and aliphatic emissions have roughly the same temporal profile. Emissions occur almost exclusively during engine start, whether hot or cold, and during hard acceleration. Emissions during start events occur because the exhaust catalyst has not reached the light-off temperature at which hydro-carbons are oxidized (largely to CO_2 & H_2O) and the engine is running fuel-rich. The engine will run rich to ensure volatilization of enough fuel for combustion, because prior to

warm-up fuel will not evaporate efficiently on the time scale of the engine combustion cycle. Because the catalyst has minimal effect prior to warm-up, the decrease in peak magnitudes for newer vehicles is largely attributed to more efficient fuel delivery programs, aided in part by better engine sensors (temperature and oxygen). Fuel delivery early in the cold-start phase appears to decrease emissions by roughly a factor of 6, judging from peak CVS concentrations (3200−500 ppb). The duration of the emissions during cold start depends on time to catalyst light-off. Figure 3 shows that older vehicles require up to 250 s for full catalyst efficiency, while new vehicles reach full conversion of hydrocarbons in close to 45 s. The reductions in duration and peak emissions are both approximately a factor of 5 to 6. This suggests that improvements in both fuel delivery and catalyst warm up contribute significantly to reductions in cold start emissions.

3.2.2. Incomplete Combustion Emissions. Species formed from incomplete combustion (e.g., acetaldehyde) generally have a similar temporal profile to the fuel components (BTEX and hydrocarbons). However, malfunctioning vehicles such as the LEV II vehicle, with high hot-stabilized and hot-start emissions of incomplete combustion compounds, have different time profiles (Figure 3). The PZEV vehicle shows a short burst during cold-start for both benzene and acetaldehyde, with nearly overlapping traces. The LEV II vehicle shows a slightly longer initial burst for both benzene and acetaldehyde followed by near-zero acetaldehyde emissions and further bursts of benzene emissions. Emissions for other incomplete combustion products monitored by PTR-MS (e.g., acetonitrile, isoprene, styrene) show the same temporal pattern as acetaldehyde. The oldest vehicle (T0), which had significant hot- and cold-start emissions, had the same trend for all observable compounds. The emissions from the LEV II vehicle indicate a poorly functioning catalyst. The LEV II emission burst at ∼300 s is due to hard acceleration, when excess fuel is delivered to the engine. At this point in the drive cycle, both the engine and the catalyst are warm, and we can assume combustion is near-optimal, minimizing the output of acetaldehyde. The differing time profiles for incomplete combustion compounds and fuel-derived compounds are further evidence of poorly functioning emissions controls. These results suggest that emissions factors for aging vehicles will vary by species and how they are formed.

3.3. Cold-Start Emissions. The importance of cold-starts from all vehicles to the total in-use fleet emissions has been clearly demonstrated in dynamometer tests.[4,5,35,36] On-road tests suggest that extreme emissions from a small portion of vehicles that have emissions control systems in catastrophic failure may outweigh the emissions from all other vehicles on the road, including cold-start emissions. This is possible because these vehicles emit continuously, even after the engine and catalyst are hot. The vehicle fleet tested here had a wide range of cars, including a very old vehicle (24 yrs, Tier 0), a poorly functioning and moderately aged vehicle (6 yrs, LEV II), and multiple brand new vehicles that meet the most stringent emission standards (<1yr, PZEV). We combine our new data with data from previous measurement campaigns to project how the future vehicle fleet will be affected by cold-start emissions.

The ratio of total cold start emissions to the hot-stabilized emissions per mile, γ, gives the number of miles a vehicle would need to travel between cold-starts before hot-stabilized emissions would exceed cold-start emissions.[4] The cold-start emissions used in this analysis are the emissions during the first

300 s of operation (full bag 1 of UC). In Figure 4 we compare γ for all vehicle classes tested for a range of chemical species,
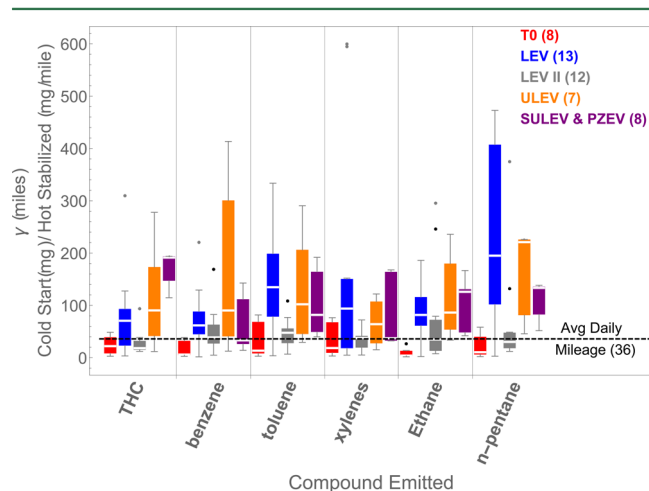
Figure 4. γ values, based on the UC test protocol, are shown for a range of species and vehicle classes. The dashed line emphasizes that the median values for most vehicle classes and types of compounds are above 36 miles, the average total daily mileage among U.S. drivers.

including THC, benzene, toluene, xylenes, ethane, and *n*-pentane. The speciated data are from GC measurements. Measurements for Tier 0, LEV I, and LEVII vehicles include both new measurements and those from previous studies.[13]

Median values of γ for NMOG are almost always greater than 30 miles, except for the oldest Tier 0 vehicles. THC emissions have a striking trend in γ values, increasing nearly an order of magnitude to reach 200+ miles for the newest emissions controls. BTEX and selected hydrocarbons (ethane and *n*-pentane) show less of a trend in γ with vehicle emissions certification, but emissions standards specify reductions in the magnitude of THC over the full driving protocol, so technologies are not necessarily expected to specifically control for cold start emissions and specific species. A typical commuter will have two cold starts, one for each direction of their commute. Accounting for both cold starts, a commuter would need to travel a minimum of 60 miles for hot running emissions to equal total cold start emissions for all exhaust compounds, for most compounds this distance is much further. In the U.S., the average total driving distance is 36 miles per day, with fewer than 10% of trips more than 50 miles in length.[37] Furthermore, vehicles with ages 20 years or greater, which encompasses Tier 0 vehicles, comprise less than 10% of the U.S. passenger car fleet.[38] This means that cold-start emissions of most NMOG species dominate total-trip emissions in the US for a majority of the in-use fleet.

We present results for several scenarios of the contribution of cold start emissions to average driving trip emissions in SI Table S7. The average trip length as of the most recent transportation survey data, commute or otherwise, is 11.8 miles.[37] Including γ values across all vehicle classes, the average contribution of cold-start emissions to total commute emissions, for all species emitted, is more than 90%. Using the lower quartile instead of the average, cold-start emissions will still be above 70% of average commute emissions. Excepting mountainous areas, which will have elevated hot stabilized emissions, the scenarios where long distances are driven will likely have lower incidences of hard acceleration,

effectively making γ values even higher. The worst case vehicles, which are all Tier 0 or Tier I vehicles, have around 10−20% of emissions due to cold starts. These vehicles are either already in the far end of the vehicle age distribution (20+ years) or soon will be. These vehicles are also not contained in the lower quartile of the respective classes. This suggests that vehicles strongly dominated by hot-stabilized emissions are less than 3% of the current in-use fleet. The above analysis relies on the ability of the UC test to reflect real-world driving (aggressiveness, length of soak periods, ambient temperature, etc.). Within the limit of the UC cycle representing US driving patterns, specifically commuting, the majority of the in-use fleet is already dominated by cold starts, and only a few percent of the fleet will have significant hot-stabilized emissions compared to cold start emissions in the next several years.

ENVIRONMENTAL IMPLICATIONS

NMOG emissions from vehicles will continue to decrease beyond the significant reductions shown above. New LEV III regulations will require emissions reductions of about 75% in the sum of NMOG and NO_x in the coming decade. The work shown here guides expectations in the composition and temporal and spatial trends these further reductions will have on emissions. Future emissions for all species from nearly all vehicles will be dominated by cold starts, occurring as a short burst that decreases in both magnitude and duration. These trends are now supported over a wide range of vehicle makes and years by combining new measurements and reanalysis of previous measurements. Newer vehicles can be expected to have their emissions further compressed into discrete events, namely cold starts and hard accelerations, and the current fleet, as vehicles are retired, will have this same trajectory. Warm-up times are already in the range of 30−40 s at moderate temperatures of about 70 °F in dynamometer tests, so an increase of just 10 s, easily caused by near freezing temperatures, is significant. This sensitivity to ambient temperature is likely to increase for newer technologies with shorter overall warm up times. The last 20+ years of innovation in emissions controls technology have not significantly changed the composition of NMOG emissions, as evidenced by the mass fraction of BTEX in the total emissions and the general mass spectra observed in the PTR-MS. This is true for both unburned fuel compounds and oxidized compounds not found in fuel. Emissions of all NMOG compound classes have the same dependence on engine activity for properly functioning vehicles, though poorly functioning vehicles may show emissions that have compositions more strongly dependent on driving conditions. In addition, the change in the BTEX profile from fuel to exhaust has also remained fairly constant with advances in emissions control technology. The total of our observations suggest that future NMOG vehicle emissions will likely not have drastic changes in composition and will become much more spatially and temporally correlated with cold starts, and the main emissions from vehicles, though greatly reduced, will become increasingly located where people live in the morning and where they work in the evening.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04513.

Vehicle details, comparison of PTR-MS to GC results, further emissions details with mass spectra, and figures for the contribution of cold starts to real-world driving (PDF)

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Notes
The authors declare no competing financial interest.

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