https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

Atmospheric Chemistry and Physics Discussions

Measurement report: Distinct Emissions and Volatility Distribution of Intermediate Volatility Organic Compounds from on-road Chinese Gasoline Vehicle: Implication of High Secondary Organic Aerosol Formation Potential

Rongzhi Tang[1,#], Quanyang Lu[2,#], Song Guo[1,3,*], Hui Wang[1], Kai Song[1], Ying Yu[1], Rui Tan[1], Kefan Liu[1], Ruizhe Shen[1], Shiyi Chen[1], Limin Zeng[1], Spiro D. Jorga[2], Zhou Zhang[4], Wenbin Zhang[4], Shijin Shuai[4], Allen L. Robinson[2,*]

1 State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, PR China

2 Department of Mechanical Engineering and Center for Atmospheric Particle Studies, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

3 International Joint Laboratory for Regional Pollution Control, Ministry of Education, Beijing, 100816, PR China

4 State Key Laboratory of Automotive Safety and Energy, School of Vehicle and Mobility,Tsinghua University, Beijing, 100084, PR China

Correspondence to: S. Guo songguo@pku.edu.cn, A. Robinson:alr@andrew.cmu.edu

[#]These authors contribute equally to this work

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

Atmospheric Chemistry and Physics Discussions

Abstract

In the present work, we performed chassis dynamometer experiments to investigate the emissions and secondary organic aerosol (SOA) formation potential of intermediate volatility organic compounds (IVOCs) from an on-road Chinese gasoline vehicle. High IVOCs emission factors (EFs) and distinct volatility distribution were recognized. The IVOCs EFs for the China V vehicle ranged from 12.1 to 226.3 mg ·kg-fuel^{-1}, with a median value of 83.7 mg ·kg-fuel^{-1}, which is higher than that from US vehicles. Besides, large discrepancy in volatility distribution and chemical composition of IVOCs from Chinese gasoline vehicle exhaust is discovered, with larger contributions of B_{14}-B_{16} compounds and higher percentage of *n*-alkanes. Further we investigated the possible reasons that influence the IVOCs EFs and volatility distribution and found that fuel type, starting mode, operating cycles and acceleration rates could have an impact on the IVOCs EF. When using E10 (ethanol volume ratio of 10%, v/v) as fuel, the IVOCs EF of the tested vehicle was lower than that using commercial China standard V fuel. Cold-start operation has higher IVOCs EF than hot-start operation. Chinese Light vehicles Test Cycle (CLTC) produced 70% higher IVOCs than those from the World-wide harmonized Light-duty Test Cycle (WLTC). We found that vehicle emitted more IVOCs at lower acceleration rates, which leads to high EFs under CLTC. The only factor that may influence the volatility distribution and compound composition is the engine-aftertreatment system, which has compound and volatility selectivity in exhaust purification. These distinct characteristics in EFs and volatility may result in higher SOA formation potential in China. Using published yield data and surrogate equivalent method, we estimated SOA formation under different OA loading and NO_x conditions. Results showed that under low and high NO_x conditions at different OA loadings, IVOCs contributes more than 80% of the predicted SOA. Furthermore, we built up a parameterization method to simply estimate the vehicular SOA based on our bottom-up measurement of VOCs and IVOCs, which would provide another dimension of information when considering the vehicular contribution to the ambient OA. Our results indicate that vehicular IVOCs contribute significantly to SOA, implying that the importance of reducing IVOCs

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

when making air pollution controlling policies in urban area of China.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

1 Introduction

Atmospheric fine particulate matter has great impacts on human health, climate, and global environmental issues (Tang et al., 2018;Guo et al., 2014b;Hallquist et al., 2009;Kanakidou et al., 2005). Organic aerosols are a major component of fine particulate matter. Secondary organic aerosol (SOA), formed from multiple generations of oxidation of thousands of organic gases and vapors, contribute 30% or more of organic aerosols in different areas of the world (Zhang et al., 2007). Due to its complexity in sources and photochemical processes, SOA formation remains uncertain (Tang et al., 2019;Guo et al., 2014a).

A large discrepancy remains between modeled and measured SOA. One possible reason is missing SOA precursors. Apart from traditional SOA precursors, i.e. volatile organic compounds (VOCs), Robinson et al. (2007) proposed intermediate volatility organic compounds (IVOCs) as important contributors to SOA formation. IVOCs are less volatile than VOCs with effective saturation concentrations in the range of 10^3 to 10^6 μg/m^3(Donahue et al., 2006), roughly corresponds to the volatility range of C_{12}-C_{22} *n*-alkanes. IVOCs exist mainly in the gas phase under typical atmospheric conditions. Previous studies demonstrate that IVOCs may be important SOA precursors both in ambient air and in typical source emissions i.e. gasoline vehicles, diesel vehicles and ship emissions (Huang et al., 2018;Zhao et al., 2016, 2015;Zhao et al., 2014).

China is in a high-growth stage with rapidly increasing number of on-road vehicles (~26 fold in 25 years). This growth has created a substantial burden on air quality and human health (Hallquist et al., 2016;Hu et al., 2015). During the past few years, many researchers have studied the gases and particulate matter emissions from Chinese vehicles (Cao et al., 2016;Huang et al., 2015). However, none of these studies have reported data on IVOCs emissions from Chinese gasoline vehicles. Although Zhao et al. (2016) characterized IVOC emission in gasoline vehicles in the United States, the results may not be applicable to China given differences in vehicle technologies, operating conditions, and fuel quality. Therefore, characterizing the IVOC emissions from Chinese vehicle is of vital importance to understand the

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

contribution of IVOCs contribution to SOA formation in China(Zhao et al., 2018;Zhao et al., 2016, 2015;Zhao et al., 2014).

In this study, IVOCs emissions were measured from a China V gasoline vehicle equipped with a direct inject (GDI) engine during chassis dynamometer testing. The test matrix considered the influence of fuel type and operating conditions on the total IVOC emission factors, including a newly designed cycle designed to simulate Chinese driving conditions. All of the measurements were performed with the same gasoline vehicle in order to consistently evaluate the effects of these different factors on IVOC emissions. The emission factors (EFs), volatility and chemical speciation of IVOC emissions from different conditions were investigated, and the SOA formation potential were estimated.

2 Materials and Methods

2.1 Testing Vehicle, Fuels and Test Cycles

In this study, all measurements were performed on a vehicle chassis dynamometer (Peng et al., 2017) using an in-use light-duty gasoline direct inject (GDI) engine vehicle meeting the China V standard (similar to Euro 5). Tests were conducted with two fuels: commercial China Standard V gasoline and E10 fuel (10% ethanol by volume). The test cycles included the World-wide harmonized Light duty Test Cycle (WLTC), and the Chinese Light vehicles Test Cycle (CLTC). Furthermore, typical different acceleration rates were also tested. Detailed description and speed profiles of WLTC and CLTC are in Figure S1 in the supplementary information. The CLTC was specifically designed to simulate the driving patterns in Chinese cities while WLTC referred to the Euro VI standard and adopted as China VI testing protocol. Prior to tests, vehicles were preconditioned with an overnight soak, without evaporative canister purge. Different acceleration rates were selected based on their frequency in both CLTC and WLTC, i.e. 1.2, 3.6 6.0 km/h/s, written as ACR1.2, ACR3.6 and ACR6.0), to investigate the effects of acceleration rates on IVOC emissions. All three acceleration “cycles” last for 600 s with a maximum velocity of 70 km/h. The acceleration driving cycles were set according to the criteria of identical

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

cycle period and maximum velocity, and hence the mean velocity for each acceleration cycle is the same (Figure S2). We also measured IVOC emission factors (EFs) when the test vehicle was idling.

2.2 Sampling and Chemical Analysis

Tailpipe emissions were introduced to a constant volume sampler (CVS) that diluted the exhaust by a factor of 20 to 40. For WLTC and CLTC tests, IVOCs emissions were collected by sampling the diluted exhaust through a quartz filter followed by two tandem Tenax TA filled glass tubes (Gerstel, 6 mm OD, 4.5 mm ID glass tube filled with ~180 mg Tenax TA). Sampling tubes and transfer lines from the CVS were kept at a constant temperature (27 ± 2 ^{o}C). The flow rate for quartz filter was 10.0 L/min, and the flow rate for Tenax tube was set as 0.5 L/min. Dynamic blanks were also collected when the CVS was operated with only dilution air (no exhaust) to estimate the contribution of background organic vapors. Prior to sampling, the quartz filters were preheated to 550 ℃ in air for 6 h in clean aluminum foil using a muffle furnace to remove contaminations. Tenax tubes were preconditioned by using Tube Conditioner (BCT700, BCT Technology LTD), at 300 ℃ for 3 h in pure nitrogen with a constant flow rate of 100 mL/min. All samples were sealed after sampling and stored in freezer at -20℃.

Quartz filters and Tenax tubes were analyzed using gas chromatography/mass spectrometer (Agilent 6890GC/5975MS) equipped with a capillary column (Agilent HP-5MS, 30 m×0.25 mm) coupled to a thermal desorption system (Gerstel, Baltimore, MD). The detailed method was described in the literature by Zhao et al.(2014). Prior to analysis, 5 μl of the internal standards (*d*10-acenaphthene, *d*12-chrysene, *d*4-1,4-dichlorobenzene, *d*8-naphthalene, *d*12-perylene, *d*10-phenanthrene and 7 deuterated *n*-alkanes) were injected into each adsorbent tube to track the IVOCs recovery.

For each test, particulate matter samples were also collected using independent Teflon and quartz filters. The Teflon filters were weighted using a microbalance (Toledo AX105DR, USA) after equilibration for 24 h in an environmental controlled

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

room (temperature 20 ± 1°C, relative humidity 40 ± 3%) (Guo et al., 2010). A punch (1.45 cm^2) from each quartz filter was analyzed for organic carbon (OC) and elemental carbon (EC) via thermal-optical method using Sunset Laboratory-based instrument (NIOSH protocol, TOT) (Guo et al., 2012). VOCs were sampled in SUUMA canisters and analyzed using GC-MS with a flame ionization detector. Total hydrocarbon (THC), nitrogen oxide, CO and CO_2 emissions under operation scenarios were measured using a Horiba OBS 2200 portable emission system.

2.3 Quantification of IVOCs

Twenty IVOCs compounds were quantified using authentic standards (Table S1). However, the majority of the IVOCs mass appears as a broad hump of co-eluting hydrocarbons and oxygenated organics. These compounds could not be resolved at the molecular level and were therefore classified as an unresolved complex mixture (UCM), which were grouped based on their volatilities.

The total mass of IVOCs was determined following the method of Zhao et al. (2014) (SI) . In short, the TIC of each sample was divided in to 11 retention time bins corresponding to C_{12}-C_{22} *n*-alkanes. The total mass in each bin was estimated using the instrument response to the *n*-alkane in that bin. UCM was determined as the difference between total IVOCs and speciated IVOCs in each bin. UCM was then further classified into unspeciated branched alkanes (*b*-alkanes) and unspeciated cyclic compounds following the approach of Zhao et al. (2016) (SI).

Fuel-based IVOC emission factor (EF, mg/kg-fuel) were calculated using the carbon-mass-balance method as following

$$EF_{IVOCs}=\frac{[\Delta IVOC]}{[\Delta CO_2]} f_c$$

where [Δ IVOC] represents the background-corrected mass concentration of IVOCs, $[\Delta CO_2]$ is the background-corrected CO_2 concentration in the CVS expressed in units of carbon mass and f_c is the measured mass fraction of carbon in the gasoline (0.82).

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

3 Results and Discussion

3.1 Influence of Fuel, Starting Mode, and Operating Cycles on IVOC Emission Factors

Figure 1 depicts IVOC EFs of the tested China V gasoline vehicle and compares them with previous studies. The IVOC EFs ranged from 12.1 to 226.3 mg ŧkg-fuel^{-1}, with a median value of 83.7 mg ŧkg-fuel^{-1}. The median IVOC value was ~3 times higher than that of the US LEV-2 gasoline vehicles (21.9 mg ŧkg-fuel^{-1}), and one order of magnitude lower than diesel-fueled non-road construction machinery and a diesel-fueled large cargo vessel (971.1 and 800 mg ŧkg-fuel^{-1}, respectively) (Qi et al., 2019;Huang et al., 2018).

Figure 1 summarizes the influences of fuel type, starting mode, operating cycles and acceleration rates on the total IVOC EFs. Among all of the factors, acceleration rate has the largest influence on the IVOC EFs. As the acceleration rate increases, the IVOC EF decreases, with the median IVOC EF of ACR6.0 being one order of magnitude lower than that at idling. Qi et al. (2019) and Zhao et al. (2016) report similar results for non-road construction machinery and on-road diesel vehicles, where idling conditions emitted significantly higher IVOCs than those under higher-speed cycles. They proposed that the higher IVOC EFs at idling were the result of less efficient fuel combustion. An additional factor in these tests may be the efficiency of the catalytic converter varying with operating conditions (i.e. lower efficiency at idle operations).

When using commercial China Standard V gasoline, the median IVOC EF was 1.4 times greater than that using Ethanol gasoline, i.e. E10 (10% ethanol, v/v), with median values of 91.5, and 67.6 mg ŧkg-fuel^{-1}, respectively. The median THC EFs for gasoline and E10 were 485 and 589 mg ŧkg-fuel^{-1}, respectively, showing no significant difference.

As expected, The IVOC EFs for cold-start tests was higher (83.7 mg ŧkg-fuel^{-1}) than those for hot-start tests (58.7 mg ŧkg-fuel^{-1}). This reflects the reduced efficiency of the catalytic converter during cold-start operation. The cold-start to hot-start IVOC emission ratio is about 1.4, which is similar to the previous study (Zhao et al., 2016).

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

The median THC EFs for cold-start and hot-start tests are 556.2 and 507.8 mg kg-fuel^{-1}, respectively. Previous studies also show that cold starts have higher THC EFs than hot start operation, but cold-to-hot ratios can span a wide range due to differences in operating conditions and model years(Jaworski et al., 2018;Drozd et al., 2016). The ratio is generally larger for more modern, heavily controlled vehicles(Saliba et al., 2017;May et al., 2014).

The median IVOC EF for CLTC was about 1.7 times of that for WLTC (103.5 versus 60.9 mg kg-fuel^{-1}). Similar results were also found for THC emission, with median THC EFs for CLTC and WLTC cycle as 617.3 and 420.3 mg kg-fuel^{-1}, respectively. Previous studies also show test cycles influence THC EFs. For example, Suarez-Bertoa et al. (2015) and Marotta et al. (2015) found NEDC cycle has higher THC EFs than WLTP or WLTC cycle. One possible explanation for the differences between the CLTC and WLTC IVOC EFs is the differences in acceleration rates. A histogram of acceleration rates of the two cycles (Figure S3) shows that CLTC has frequent low acceleration process compared to WLTC. 76.9% of the CLTC has acceleration rates ranging from -1.5 to 1.5 km/h/s versus 69.6% for the WLTC. The CLTC has no acceleration rate higher than 4 km/h/s, suggesting that the gasoline vehicles frequently drive in congested conditions in China.

The results from the acceleration rate cycles suggest that the frequent low acceleration rate in CLTC is responsible for the differences of the IVOC EF between CLTC and WLTC. The effect of acceleration on IVOC EFs is probably especially important in urban areas in China, which frequently have substantial traffic congestion. These results underscore the importance of developing cycles that simulate real-world Chinese driving condition e.g. CLTC, instead of using WLTC or other cycles to get relevant emissions data.

3.2 Chemical Speciation of Chinese Vehicle IVOCs and the Relationships between Total IVOCs, POA and THC

Figure 2 and S4 compare the chemical composition of IVOC emissions from the tested China V vehicle under different operating conditions. In general, IVOC

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

chemical composition was similar across all the tests. Unspeciated IVOCs (UCM) dominates the total IVOCs mass (85.6 ±4.9%), including 65.2 ±5.2% for unspeciated cyclic compounds and 20.4 ±0.7% for unspeciated *b*-alkanes. *n*-alkanes and speciated aromatics contribute 10.9 ±4.7% and 3.5 ±1.7% of the total IVOC mass, respectively. These results are similar to previous studies. For example, Zhao et al. (2016) found the consistent composition of IVOC emissions across a wide set of vehicles.

Since the majority of the IVOC mass appears as UCM, the average mass spectra provide additional insight into its composition. A similar distribution of mass fragments was observed across all tests. Figure 2(b) shows the average IVOC mass spectrum collected during an E10 CLTC test. Mass fragments associated with aliphatic hydrocarbons (*m/z* 43, 57, 71, 85) are the most abundant followed by those associated with aromatics (*m/z* 91, 105 and 119 for alkylbenzenes (Pretsch et al., 2013), and *m/z* 115, 165, 189 for poly aromatic species) (Dall'Osto et al., 2009;Spencer et al., 2006).

Figures 2(c) and (d) exhibit the contribution of selected mass fragments in low and high volatility ranges, i.e. B_{12}-B_{16} and B_{17}-B_{22}. Aliphatic fragments are higher than aromatics fragments in both B_{12}-B_{16} and B_{17}-B_{22} bins. Compared to the higher volatility (B_{12}-B_{16}) bins, the ratio of selected aromatic to aliphatic fragments is lower in the lower volatility (B_{17}-B_{22}) bins (0.8 versus 1.7) which suggests different weighting of compounds in different volatility range. Therefore, unspeciated IVOC UCM in B_{12}-B_{16} are predominantly aromatics while B_{17}-B_{22} are more abundant in cyclic alkanes.

Figure 3 and S5 shows the volatility distribution of IVOC emissions in the 11 retention-time bins (B_{12}-B_{22}). IVOC emissions are more heavily weighted towards the more volatile end of the distribution, with more than 50% of the emissions in B_{12}-B_{14} bins. After B_{14}, the IVOC emission decreases significantly.

Although the IVOC EFs varied by an order of magnitude across the set of tests (Figure 1), the volatility distributions of the emissions were largely the same. When the vehicle is fueled by gasoline, the median IVOC fractions in the B_{12}-B_{14} bins are slightly higher than when fueled by E10. Cold-start having a higher median

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

percentage of IVOC in B_{12}-B_{14} bins compared to hot-start. No distinct differences in volatility differences between the CLTC and WLTC. Compared with idling condition, acceleration cycles have higher median percentage of IVOC in lower volatility bins (B_{17}-B_{22}), similar to previous studies (Qi et al., 2019;Cross et al., 2015).The modest variations of volatility distributions of the IVOCs emissions may be due to differences in combustion efficiency and/or catalytic converter efficiency as a function of volatility.

Previous studies have used different scaling approaches to estimate IVOC emissions using other primary emission data, e.g. POA, NMHC (Murphy et al., 2017;Woody et al., 2016;Koo et al., 2014). However, these ratios depend on fuel, engine technology and operating conditions (Lu et al., 2018).Therefore, it is important to quantify the relationships between IVOCs and other pollutants using data collected from Chinese vehicles. Our results show that the IVOC-to-THC ratio does depend on fuel composition. The average IVOC-to-THC ratios for gasoline-fueled and E10-fueled gasoline vehicle are 0.07 ± 0.01(R^2 = 0.87) and 0.11 ± 0.02 (R^2 = 0.78), respectively (Figure S6). The IVOC-to-THC ratios in this study are higher than US vehicles (IVOC-to-NMHC of 0.04) (Zhao et al., 2016) but much lower than diesel fueled vehicles (IVOC-to-THC of 0.67) (Huang et al., 2018). The IVOC-to-POA ratio was 5.12 ± 1.30 across all tests, but with only modest correlation (R^2 of 0.66 for gasoline-fueled vehicle and 0.43 for E10-fueled vehicle). This ratio is similar to US data for gasoline vehicles. The correlation of IVOC to THC or POA in our dataset is lower than that of the on-road gasoline and diesel vehicles measured in US. This may be caused to the US data are from a large fleet of vehicles while our data is from a single vehicle operated over a range of conditions

3.3 High Emission Factors and Distinct Volatility Distributions of IVOCs from Chinese Gasoline Vehicles

Figure 4 presents PM, NO_x, THC and IVOC EFs of the tested gasoline vehicle (China V) and compares them to US vehicles tested by Zhao et al. (Zhao et al., 2016;May et al., 2014) For this comparison, we combined all of the CLTC and WLTC

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

data together. The US vehicles are grouped by model year where pre-LEV refers to vehicles manufactured prior to 1994, LEV-1 represents vehicles manufactured between 1994-2003, and LEV-2 indicates vehicles manufactured between 2004-2012.

The emissions of NO_x and THC from tested vehicle are comparable with those from the newer (LEV-2) US vehicles tested by May et al. (Zhao et al., 2016;May et al., 2014). However, PM EF (44.8 mg kg-fuel^{-1}) of the tested vehicle is higher than the LEV-2 vehicles tested (17.0 mg kg-fuel^{-1}). It is comparable to a pre-LEV vehicle (61.0 mg kg-fuel^{-1}). This suggests that stringent emission implemented by Chinese government have been effective at controlling NO_x and THC, but inefficient to PM emissions.

The IVOC EFs for the tested China V vehicle is between the US Pre-LEV and LEV-1 vehicle. Therefore, Chinese regulations also appear to be ineffective at controlling IVOC emissions. The IVOC-to-THC ratio measured here (0.07 for gasoline and 0.11 for E10) is higher than US vehicles (0.04), which means that IVOCs contribute a larger fraction of the THC emissions from the China V than from the US vehicles. A detailed comparison of the individual VOC emissions between China V and US LEV-2 vehicles is in SI (Table S8).

UCM accounts for large fraction of IVOCs for both China V and US gasoline vehicles. However, the speciated compounds exhibit different characteristics. The China V exhaust has less speciated IVOC aromatic compounds (3.5%) and more alkanes (10.9%) compared to US exhaust (12.9% and 2.5%, respectively). This is also reflected by the IVOC mass spectrum, where Chinese vehicle exhaust has higher *m/z* 43, 57, 71, 85 signals. In addition, the specific aromatics mass fragments were not the same for China V and US IVOC emissions. For example, the dominant aromatics fragments in US gasoline exhaust are *m/z* 128, 119, 105, 133 versus *m/z* 135, 91, 181, 189 for China V. (Fig. 2c and d).

Figure 3 compares the volatility distribution of the IVOC emissions from the China V and US vehicles. There are significant differences of volatility distribution between China V and US vehicles. Both distributions decrease with the increase of the retention time, but the IVOC volatility distribution of US vehicle exhaust exhibits

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

heavier weight of lower volatility bin, i.e. B_{12} bin compared to the China V vehicle. In US exhaust the B_{12} fraction is more than double of the B_{13}. However, the contributions of B_{12}-B_{14} bin volatility bins are comparable for Chinese vehicle exhaust. US vehicle exhaust has a similar IVOC volatility distribution to the unburned gasoline, indicating that the evaporate of IVOCs from fuel is non neglectable.

The differences between the IVOC volatility distribution between the Chinese vehicle exhaust and unburned gasoline were further investigated. The higher emission factor and broader distribution of IVOCs in exhaust from China V compared with US vehicles may be due to differences in fuel composition, operating conditions and engines and after-treatment technology. Lu et al. (2018) demonstrated that IVOC emissions depend strongly on fuel composition. In our study, IVOCs contributed ~2.0 wt% (2.1 wt% for gasoline, 1.9 wt% for E10) of the total fuel mass, which is ~60% higher than the California fuel (E10, 1.2 wt%)(Gentner et al., 2012). Therefore, the higher IVOC fractions in China V exhaust (e.g. IVOC-to-THC ratio of 0.07 and 0.11 versus 0.04 in US exhaust) may lead to higher amounts of IVOCs in China V gasoline. When considering volatility distribution, Zhao et al. (2016) and Lu et al. (2018) reported similar distributions of IVOC between gasoline vehicle exhaust and unburned fuel, which demonstrates the significant influence of unburned fuel on exhaust volatility distribution. However, the volatlity distribution of the China V gasoline vehicle exhaust are different from that of the unburned fuel (Figure 3). The difference might be related to the operating conditions and engine-aftertreatment system.

Although operating conditions strongly influence the total IVOC EFs (Figure 1), Figure 3 indicates the volatility distribution of the IVOCs emissions were largely consistent across the set of test conditions. Therefore, operating conditions cannot explain the difference in the IVOC volatility distribution between the China V vehicle, unburned gasoline, and the US vehicles.

The engine-aftertreatment system also influences IVOC emissions (Drozd et al., 2019;Alam et al., 2019;Zhao et al., 2018;Saliba et al., 2017). In order to investigate the efficiency of after-treatment system, we normalized the IVOC distributions of the

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

fuel and exhaust to the sum of C_8-C_{10} *n*-alkanes. It is believed that the C_8-C_{10} *n*-alkanes can serve as the indicators for VOCs in fuel (Lu et al. 2018). For both US and the China V vehicles, IVOCs are enriched in the exhaust relative to the fuel. However, the enrichment factor is much smaller in Chinese exhaust with a median value of 4.0 than that for US vehicles (median value = 8.5) (Lu et al., 2018). The enrichment factor also varies with different compounds, with the enrichment factors of *n*-alkanes (9.3)＞*b*-alkanes (6.6)＞unspeciated cyclic ompounds (3.1)＞aromatics (0.4). These results are consistent with previous studies stating that the aftertreatment devices have different removal efficiency towards different compounds (Ma et al., 2019;Hasan et al., 2018;Hasan et al., 2016;Alam and Harrison, 2016). Our results suggest that the Chinese three-way catalytic converter has compound dependent efficiency (better removal of aromatics compared to alkanes) which might explain the difference in compound composition between Chinese and US vehicle exhaust. Furthermore, Fig. S9 shows that the catalytic converter has different removal capacity towards different volatility bins, in which $B_{14\text{-}16}$ works much worse compared to other volatility bins i.e. B_{12}. Consequently, the SOA formation would be relatively high. In sum, the compound dependent capacity and lower B_{14}-B_{16} removal efficiency of Chinses TWC is responsible for the volatility distribution differences between China V and US vehicles shown in Figure 3.

After considering all the factors above, we can draw the conclusion that fuel type, starting mode and operating conditions can all affect the IVOCs EFs. The only factor that impacts the volatility distribution is engine-aftertreament system.

3.4 Estimation of SOA Production from Chinses Vehicle Emission

With the measured IVOC and VOC emissions, we estimated the SOA formation potential by using the yield method as following (Yuan et al., 2013):

$$\Delta SOA/\Delta CO = \sum ER_{[HC]_i} \times \left(1 - e^{-(k_{OH,i} - k_{CO}) \times [OH] \times \Delta t}\right) \times Y_i$$

In which, $ER_{[HC]_i}$ is the emission ratio of SOA precursor i (mg·kg-fuel^{-1}); $k_{OH,i}$ is the OH reaction rate constant of precursor i at 298K (cm^3·molecules^{-1} s^{-1}); k_{CO} is the OH reaction constant of CO at 298 K (2.4×10^{-13} cm^3·molecules^{-1} s^{-1}); [OH] is the

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

OH mixing ratio, which is assumed to be 1.5×10^{6} molecules cm^{3} (Lu et al., 2019); Δt is photochemical age (h); and Y_i is the SOA yield determined from chamber studies. Previous studies have shown that the SOA yield of individual hydrocarbon can be influenced by NO_x level, due to the competition reactions among RO_2 radicals, NO and HO_2 radicals. Usually SOA yields under low NO_x condition are independent on the OA loading. However, under high NO_x condition, SOA yields highly depend on OA mass concentration, which can be described using two-product or multi-products model (Presto et al., 2010;Chan et al., 2009;Ng et al., 2007). In this study, we estimated SOA formation under low and high NO_x conditions with OA concentration of 10, 20, 80 $\mu g\cdot m^{-3}$ to represent the influence of NO_x level and OA loading on SOA formation.

In this estimation, we include speciated C_6-C_9 single ring aromatics (SRAs) as typical VOCs for SOA precursors, and the corresponding k_{OH} and SOA yields are extrapolated according to two-product relationship from chamber studies (see SI) (Ng et al., 2007). The SOA yields under low and high NO_x condition, and the OH reaction rates of speciated IVOCs and SRAs are from the previous studies (see SI) (Presto et al., 2010;Lim and Ziemann, 2009;Chan et al., 2009). In brief, surrogate species were used to represent the unspeciated *b*-alkanes and cyclic compounds in each of the volatility bins.

Figure 5 shows the POA emission and estimated SOA production under different operating conditions and NO_x level after 48 h of photo-oxidation. The estimated SOA/POA ratio is between 4.0 to 5.0 under low NO_x condition, and the SOA-to-POA ratios ranged from 1.8-2.2 to 3.8-4.4 when the OA loading increased from 10 $\mu g\cdot m^{-3}$ to 80 $\mu g\cdot m^{-3}$ under high NO_x condition. The OA enhancement under low NO_x condition is similar to that under high NO_x condition with the OA loading of 80 $\mu g\cdot m^{-3}$. Considering the high POA concentration and SOA formation capacity of Chinese gasoline vehicles, the SOA/POA ratios at 80 $\mu g\cdot m^{-3}$ are considered as a lower estimation. Compared with OA enhancement from US studies (~3.6) (Zhao et al., 2016), our results showed higher SOA formation potential both under low and high NO_x conditions for Chinese gasoline vehicles.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

Scenario-based analysis showed similar tendency of SOA formation potential at different OA loading under low and high NO_x condition. Comparable SOA formation was estimated using gasoline and E10 as fuel. However, the OA enhancement factor for E10 is higher than that of gasoline, suggesting that although the ongoing policy of ethanol gasoline will not exacerbate the POA and SOA pollution in China, the OA enhancement capacity of E10 could not be neglected. More research should be done to evaluate the effectiveness of using E10 as surrogate to reduce the air pollution in China. Cold-start operation has higher SOA potential with higher OA enhancement factor than hot-start, due to the higher precursors EFs caused by the reduced catalytic converter effectiveness below its light off temperature(Drozd et al., 2019). The IVOC EFs, the estimated SOA production and SOA/POA of CLTC are all higher than those of WLTC, which further demonstrates the higher SOA formation potential of Chinese gasoline vehicles under typical driving conditions in China.

Figure S10 presents the contribution of different classes of precursors on the SOA production after 48 h of photo-oxidation under different OA loading and NO_x condition. The relative contributions of different chemical classes were similar across the different conditions, with the largest contribution from unspeciated cyclic IVOCs. This is different from the US gasoline vehicle SOA (Zhao et al., 2016) in which single ring aromatics contributes the most.

3.5 Establishing the Estimation Method of SOA formation from Chinese Gasoline Vehicles

In this section, we tried to establish parameterization methods to provide simple estimations of gasoline vehicle SOA based on our measurements of VOCs and IVOCs.

Figure S11 shows the average predicted SOA-to-POA ratio as the function of photo-oxidation time under different OA loading and NO_x conditions. In general, SOA exceeds POA after first a few hours of oxidation, and then keeps constant after ~24 h. The SOA/POA ratio is influenced by OA concentration, NO_x level and the photochemical age (OH exposure). At a certain OA loading and OH exposure,

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

SOA/POA ratio can be estimated, and then be used to quantify the contributions of gasoline vehicle SOA to the ambient OA. Therefore, we parameterized the SOA/POA variation under different OA and NO_x condition using three-parameter-based logarithm equation, i.e. $y=a-b\times\ln(t+c)$, in which t represents the equivalent photochemical age (assume that the OH concentration is 1.5×10^6 molecules cm^3) and a, b, c can be described using three-parameter logarithm equation $y=m-n\times\ln([\text{OA concentration}]+p)$. Table 1 shows the parameterization results of compounds-based SOA/POA variation under the different OA and NO_x condition.

Table 1 Coefficient of parameterization between SOA/POA and photochemical age

SOA/POA	Low NO_x condition	High NO_x condition		
		m	n	p
a	-0.62	0.46	0.22	9.8
b	1.34	0.27	0.33	2.58
c	0.58	0.13	-0.09	3.35
Unspeciated cyclic compounds				
a	-0.15	0.26	0.09	21.76
b	0.72	0.086	0.18	0.46
c	0.11	-0.278	-0.083	24.42
Unspeciated b-alkanes				
a	-0.11	0.47	0.111	87.54
b	0.17	0.15	0.070	12.36
c	0.84	-0.17	-0.21	41.97
aromatics				
a	-0.03	-0.023	-0.0098	40.52
b	0.03	0.012	0.007	17.27
c	-1.00	-1.02	-0.021	-10.00
n-alkanes				
a	-0.05	0.0067	0.013	-2.38
b	0.11	0.019	0.030	-0.52

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

c	0.48	0.15	-0.058	29.18
Single ring aromatics				
a	-0.51	0.28	0.17	5.47
b	0.35	0.03	0.059	-2.29
c	3.92	2.80	-1.29	10.84

The above photochemical-based parameterization method provides a conservative way to quantify the evolution of SOA from Chinese gasoline vehicle VOCs and IVOCs oxidation. However, there are still some uncertainties which may lead to discrepancies between predicted and measured SOA. In general, positive or negative artifacts of quartz filters, *n*-alkane equivalent method in estimating the IVOCs concentration, uncertainty in SOA yield, surrogate method to substitute SOA yield and k_{OH} for UCM and lack of semi-volatile organic compounds will exert influence on the SOA prediction.

4 Atmospheric Implications

We measured the VOCs, IVOCs and POA emitted from a China V light duty gasoline vehicle across a wide range of operating conditions. Compared with US LEV-2 gasoline vehicle, China V vehicle emits three times higher IVOCs. Besides, the IVOC emissions from the China V vehicle have a much broader volatility distribution than that from US vehicles. These characteristics imply that IVOCs could act more important SOA precursors in China than those in the US. For Chinese gasoline vehicles, although the magnitude of the emission of IVOCs and VOCs can vary, their relative contribution to SOA production is similar across the set of operating conditions examined here due to the similar volatility distributions. As a result, the key to control SOA formation of gasoline vehicles is to reduce the total IVOC EFs by upgrading of emissions controls. In addition, reducing congestion and other low speed operating modes would also be effective at reducing emissions (Figure 1 and 5).

Based on our results, we roughly estimate the vehicle IVOC emissions in China. Till the end of 2018, the HC emission of gasoline vehicles in China was 0.23 Mt,

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

accounting for more than 70% of the total vehicle emissions. Using an IVOC/THC ratio of 0.09 that is obtained in our work, we estimate that the vehicle IVOC emissions in China are 0.03 Mt (30 Gg), in which 20 Gg is attributed to gasoline vehicles. One should note that this estimation is a conservative value, since we consider all vehicles as gasoline vehicles, and all of them meet the China V standard. Considering the IVOC/NMHC ratio of diesel vehicles could be much higher than that of the gasoline vehicles(Zhao et al., 2016, 2015). This may also lead to an underestimation.

Our results show that using a Chinese real-world test protocol CLTC will result in substantially higher IVOC emissions compared with WLTC which might have close relationship with frequent idling and low acceleration condition. Therefore, when driving at typical Chinese condition where traffic congestion frequently occur, the IVOCs emission from Chinese gasoline vehicles would be much higher than the current limited emission inventory. Our results indicate simply controlling the THC, NO_x and primary PM emissions may be insufficient in the aspect of controlling particle pollution. Reducing IVOC emissions should also be taken into consideration due to their high contribution to SOA formation, which is more important than primary organic aerosol. Suggested controlling ways include upgrading the fuel quality and engine-after treatment system, and reducing the traffic congestion.

Acknowledgement

This research is supported by the National Natural Science Foundation of China (No. 41977179，51636003，21677002，91844301), the Open Research Fund of State Key Laboratory of Multi-phase Complex Systems (MPCS-2019-D-09). ALR and QY received financial support from the Center for Air, Climate, and Energy Solutions (CACES), which was funded by Assistance Agreement No. RD83587301 awarded by the U.S. Environmental Protection Agency. It has not been formally reviewed by EPA. The views expressed in this document are solely those of authors and do not necessarily reflect those of the Agency. EPA does not endorse any products or commercial services mentioned in this publication.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

References

Alam, M. S., and Harrison, R. M.: Recent advances in the application of 2-dimensional gas chromatography with soft and hard ionisation time-of-flight mass spectrometry in environmental analysis, Chemical Science, 7, 3968-3977, 10.1039/c6sc00465b, 2016.

Alam, M. S., Zeraati-Rezaei, S., Xu, H., and Harrison, R. M.: Characterization of Gas and Particulate Phase Organic Emissions (C9–C37) from a Diesel Engine and the Effect of Abatement Devices, Environmental science & technology, 53, 11345-11352, 2019.

Cao, X., Yao, Z., Shen, X., Ye, Y., and Jiang, X.: On-road emission characteristics of VOCs from light-duty gasoline vehicles in Beijing, China, Atmospheric Environment, 124, 146-155, https://doi.org/10.1016/j.atmosenv.2015.06.019, 2016.

Chan, A. W. H., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crounse, J. D., Kuerten, A., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs), Atmospheric Chemistry and Physics, 9, 3049-3060, 10.5194/acp-9-3049-2009, 2009.

Cross, E. S., Sappok, A. G., Wong, V. W., and Kroll, J. H.: Load-Dependent Emission Factors and Chemical Characteristics of IVOCs from a Medium-Duty Diesel Engine, Environmental Science & Technology, 49, 13483-13491, 10.1021/acs.est.5b03954, 2015.

Dall'Osto, M., Harrison, R., Coe, H., and Williams, P.: Real-time secondary aerosol formation during a fog event in London, Atmospheric Chemistry and Physics, 9, 2459-2469, 2009.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environmental Science & Technology, 40, 2635-2643, 10.1021/es052297c, 2006.

Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Weber, R. J., Chang, M. C. O., Maldonado, H., Sardar, S., Robinson, A. L., and Goldstein, A. H.: Time Resolved Measurements of Speciated Tailpipe Emissions from Motor Vehicles: Trends with Emission Control Technology, Cold Start Effects, and Speciation, Environmental Science & Technology, 50, 13592-13599, 10.1021/acs.est.6b04513, 2016.

Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Chang, M. C. O., Maldonado, H., Sardar, S., Weber, R. J., Robinson, A. L., and Goldstein, A. H.: Detailed speciation of intermediate volatility and semivolatile organic compound emissions from gasoline vehicles: effects of cold starts and implications for secondary organic aerosol formation, Environmental Science & Technology, 53, 1706-1714, 10.1021/acs.est.8b05600, 2019.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, Proceedings of the National Academy of Sciences of the United States of America, 109, 18318-18323, 2012.

Guo, S., Hu, M., Wang, Z. B., Slanina, J., and Zhao, Y. L.: Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: implication of regional secondary formation, Atmospheric Chemistry and Physics, 10, 947-959, 2010.

Guo, S., Hu, M., Guo, Q., Zhang, X., Schauer, J. J., and Zhang, R.: Quantitative evaluation of emission controls on primary and secondary organic aerosol sources during Beijing 2008 Olympics,

Atmospheric Chemistry and Physics, 13, 8303-8314, 2012.

Guo, S., Hu, M., Shang, D. J., Guo, Q. F., and Hu, W. W.: Research on Secondary Organic Aerosols Basing on Field Measurement, Acta Chimica Sinica, 72, 145-157, 10.6023/a13111169, 2014a.

Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., Zeng, L., Molina, M. J., and Zhang, R.: Elucidating severe urban haze formation in China, Proceedings of the National Academy of Sciences of the United States of America, 111, 17373-17378, 10.1073/pnas.1419604111, 2014b.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and Physics, 9, 5155-5236, 2009.

Hallquist, M., Munthe, J., Hu, M., Wang, T., Chan, C. K., Gao, J., Boman, J., Guo, S., Hallquist, A. M., and Mellqvist, J.: Photochemical smog in China: scientific challenges and implications for air-quality policies, National Science Review, 3, 401-403, 2016.

Hasan, A. O., Abu-jrai, A., Al-Muhtaseb, A. a. H., Tsolakis, A., and Xu, H.: Formaldehyde, acetaldehyde and other aldehyde emissions from HCCI/SI gasoline engine equipped with prototype catalyst, Fuel, 175, 249-256, https://doi.org/10.1016/j.fuel.2016.02.005, 2016.

Hasan, A. O., Elghawi, U. M., Al-Muhtaseb, A. a. H., Abu-jrai, A., Al-Rawashdeh, H., and Tsolakis, A.: Influence of composite after-treatment catalyst on particle-bound polycyclic aromatic hydrocarbons–vapor-phase emitted from modern advanced GDI engines, Fuel, 222, 424-433, https://doi.org/10.1016/j.fuel.2018.02.114, 2018.

Hu, M., Guo, S., Peng, J., and Wu, Z.: Insight into characteristics and sources of PM2.5 in the Beijing–Tianjin–Hebei region, China, National Science Review, 2, 257-258, 2015.

Huang, C., Wang, H., Li, L., Wang, Q., Lu, Q., De Gouw, J., Zhou, M., Jing, S., Lu, J., and Chen, C.: VOC species and emission inventory from vehicles and their SOA formation potentials estimation in Shanghai, China, Atmospheric Chemistry and Physics, 15, 11081-11096, 2015.

Huang, C., Hu, Q., Li, Y., Tian, J., Ma, Y., Zhao, Y., Feng, J., An, J., Qiao, L., Wang, H., Jing, S. a., Huang, D., Lou, S., Zhou, M., Zhu, S., Tao, S., and Li, L.: Intermediate Volatility Organic Compound Emissions from a Large Cargo Vessel Operated under Real-world Conditions, Environmental Science & Technology, 52, 12934-12942, 10.1021/acs.est.8b04418, 2018.

Jaworski, A., Kuszewski, H., Ustrzycki, A., Balawender, K., Lejda, K., and Woś, P.: Analysis of the repeatability of the exhaust pollutants emission research results for cold and hot starts under controlled driving cycle conditions, Environmental Science and Pollution Research, 25, 17862-17877, 10.1007/s11356-018-1983-5, 2018.

Kanakidou, M., Seinfeld, J., Pandis, S., Barnes, I., Dentener, F., Facchini, M., Dingenen, R. V., Ervens, B., Nenes, A., and Nielsen, C.: Organic aerosol and global climate modelling: a review, Atmospheric Chemistry and Physics, 5, 1053-1123, 2005.

Koo, B., Knipping, E., and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, Atmospheric Environment, 95, 158-164, https://doi.org/10.1016/j.atmosenv.2014.06.031, 2014.

Lim, Y. B., and Ziemann, P. J.: Effects of molecular structure on aerosol yields from OH radical-initiated reactions of linear, branched, and cyclic alkanes in the presence of NO x,

Environmental science & technology, 43, 2328-2334, 2009.

Lu, K., Guo, S., Tan, Z., Wang, H., Shang, D., Liu, Y., Li, X., Wu, Z., Hu, M., and Zhang, Y.: Exploring atmospheric free-radical chemistry in China: the self-cleansing capacity and the formation of secondary air pollution, National Science Review, 6, 579-594, 2019.

Lu, Q., Zhao, Y., and Robinson, A. L.: Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions, Atmospheric Chemistry and Physics, 18, 17637-17654, 2018.

Ma, R., He, X., Zheng, Y., Zhou, B., Lu, S., and Wu, Y.: Real-world driving cycles and energy consumption informed by large-sized vehicle trajectory data, Journal of Cleaner Production, 223, 564-574, https://doi.org/10.1016/j.jclepro.2019.03.002, 2019.

Marotta, A., Pavlovic, J., Ciuffo, B., Serra, S., and Fontaras, G.: Gaseous Emissions from Light-Duty Vehicles: Moving from NEDC to the New WLTP Test Procedure, Environmental Science & Technology, 49, 8315-8322, 10.1021/acs.est.5b01364, 2015.

May, A. A., Nguyen, N. T., Presto, A. A., Gordon, T. D., Lipsky, E. M., Karve, M., Gutierrez, A., Robertson, W. H., Zhang, M., Brandow, C., Chang, O., Chen, S. Y., Cicero-Fernandez, P., Dinkins, L., Fuentes, M., Huang, S. M., Ling, R., Long, J., Maddox, C., Massetti, J., McCauley, E., Miguel, A., Na, K., Ong, R., Pang, Y. B., Rieger, P., Sax, T., Truong, T., Vo, T., Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles, Atmospheric Environment, 88, 247-260, 2014.

Murphy, B. N., Woody, M. C., Jimenez, J. L., Carlton, A. M. G., and Pye, H. O. T.: Semivolatile POA and parameterized total combustion SOA in CMAQv5.2: impacts on source strength and partitioning, Atmospheric Chemistry & Physics, 17, 11107-11133, 2017.

Ng, N., Kroll, J., Chan, A., Chhabra, P., Flagan, R., and Seinfeld, J.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmospheric Chemistry and Physics, 7, 3909-3922, 2007.

Peng, J. F., Hu, M., Du, Z. F., Wang, Y. H., Zheng, J., Zhang, W. B., Yang, Y. D., Qin, Y. H., Zheng, R., Xiao, Y., Wu, Y. S., Lu, S. H., Wu, Z. J., Guo, S., Mao, H. J., and Shuai, S. J.: Gasoline aromatics: a critical determinant of urban secondary organic aerosol formation, Atmospheric Chemistry and Physics, 17, 10743-10752, 10.5194/acp-17-10743-2017, 2017.

Presto, A. A., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Secondary organic aerosol formation from high-NO(x) photo-oxidation of low volatility precursors: n-alkanes, Environmental Science & Technology, 44, 2029-2034, 2010.

Pretsch, E., Clerc, T., Seibl, J., and Simon, W.: Tables of spectral data for structure determination of organic compounds, Springer Science & Business Media, 2013.

Qi, L., Liu, H., Shen, X. e., Fu, M., Huang, F., Man, H., Deng, F., Shaikh, A. A., Wang, X., Dong, R., Song, C., and He, K.: Intermediate-Volatility Organic Compound Emissions from Nonroad Construction Machinery under Different Operation Modes, Environmental Science & Technology, 53, 13832-13840, 10.1021/acs.est.9b01316, 2019.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging, Science, 315, 1259-1262, 2007.

Saliba, G., Saleh, R., Zhao, Y., Presto, A. A., Larnbe, A. T., Frodin, B., Sardar, S., Maldonado, H., Maddox, C., May, A. A., Drozd, G. T., Goldstein, A. H., Russell, L. M., Hagen, F., and Robinson, A. L.: Comparison of Gasoline Direct-Injection (GDI) and Port Fuel Injection (PFI) Vehicle Emissions:

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

Emission Certification Standards, Cold-Start, Secondary Organic Aerosol Formation Potential, and Potential Climate Impacts, Environmental Science & Technology, 51, 6542-6552, 10.1021/acs.est.6b06509, 2017.

Spencer, M. T., Shields, L. G., Sodeman, D. A., Toner, S. M., and Prather, K. A.: Comparison of oil and fuel particle chemical signatures with particle emissions from heavy and light duty vehicles, Atmospheric Environment, 40, 5224-5235, 2006.

Suarez-Bertoa, R., Zardini, A. A., Keuken, H., and Astorga, C.: Impact of ethanol containing gasoline blends on emissions from a flex-fuel vehicle tested over the Worldwide Harmonized Light duty Test Cycle (WLTC), Fuel, 143, 173-182, https://doi.org/10.1016/j.fuel.2014.10.076, 2015.

Tang, R., Wu, Z., Li, X., Wang, Y., Shang, D., Xiao, Y., Li, M., Zeng, L., Wu, Z., Hallquist, M., Hu, M., and Guo, S.: Primary and secondary organic aerosols in summer 2016 in Beijing, Atmos. Chem. Phys., 18, 4055-4068, 10.5194/acp-18-4055-2018, 2018.

Tang, R., Wang, H., Liu, Y., and Guo, S.: Constituents of Atmospheric Semi-Volatile and Intermediate Volatility Organic Compounds and Their Contribution to Organic Aerosol, PROGRESS IN CHEMISTRY, 31, 180-190, 2019.

Woody, M. C., Wong, H. W., West, J. J., and Arunachalam, S.: Multiscale predictions of aviation-attributable PM2.5 for US airports modeled using CMAQ with plume-in-grid and an aircraft-specific 1-D emission model, Atmospheric Environment, 147, 384-394, 10.1016/j.atmosenv.2016.10.016, 2016.

Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.: VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China, Atmospheric Chemistry and Physics, 13, 8815-8832, 10.5194/acp-13-8815-2013, 2013.

Zhang, Q., Jimenez, J., Canagaratna, M., Allan, J., Coe, H., Ulbrich, I., Alfarra, M., Takami, A., Middlebrook, A., and Sun, Y.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically‐influenced Northern Hemisphere midlatitudes, Geophysical Research Letters, 34, 2007.

Zhao, Y., Hennigan, C. J., May, A. A., Tkacik, D. S., de Gouw, J. A., Gilman, J. B., Kuster, W. C., Borbon, A., and Robinson, A. L.: Intermediate-Volatility Organic Compounds: A Large Source of Secondary Organic Aerosol, Environmental Science & Technology, 48, 13743-13750, 10.1021/es5035188, 2014.

Zhao, Y., Nguyen, N. T., Presto, A. A., Hennigan, C. J., May, A. A., and Robinson, A. L.: Intermediate Volatility Organic Compound Emissions from On-Road Diesel Vehicles: Chemical Composition, Emission Factors, and Estimated Secondary Organic Aerosol Production, Environmental Science & Technology, 49, 11516-11526, 10.1021/acs.est.3b02841, 2015.

Zhao, Y., Nguyen, N. T., Presto, A. A., Hennigan, C. J., May, A. A., and Robinson, A. L.: Intermediate Volatility Organic Compound Emissions from On-Road Gasoline Vehicles and Small Off-Road Gasoline Engines, Environmental Science & Technology, 50, 4554-4563, 10.1021/acs.est.5b06247, 2016.

Zhao, Y., Lambe, A. T., Saleh, R., Saliba, G., and Robinson, A. L.: Secondary organic aerosol production from gasoline vehicle exhaust: Effects of engine technology, cold start, and emission certification standard, Environmental science & technology, 52, 1253-1261, 2018.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

Figure Caption

Figure 1. IVOC emission factors measured under different conditions, i.e. different fuel type (gasoline, E10), test cycles (Chinese Light vehicles Test Cycle, CLTC, and World-wide harmonized Light-duty Test Cycle, WLTC), starting mode (hot start and cold start), and acceleration rates (acceleration rates of 1.2, 3.6 and 6.0 km/h/s). Stars indicate the EF data from US, i.e. median US LEV-2 gasoline vehicles (vehicles manufactured in 2004-2012), non-road construction machinery, and a large cargo vessel (Qi et al., 2019;Huang et al., 2018;Zhao et al., 2016). The first category "China V" is the compilation of all the EF results from all of the CLTC and WLTC tests. The boxes indicate the median value, with error bars represent one standard deviation.

Figure 2. (a) Comparison of average chemical speciation of IVOC emissions from China V vehicle and US vehicles (Zhao et al., 2016); (b) Average mass spectrum of the IVOC during a typical E10-fueled cold start CLTC test. (c-d) Box-whisker plots of the fractional contribution of selected fragments to total IVOCs signal for tested China V vehicle：(c) B_{12}-B_{16} bins; (d) B_{17}-B_{22} bins. The boxes represent the 25th and 75th percentiles with the centerline being the median. The whiskers are the 10th and 90th percentiles. Black hollow triangles represent median LEV-2 data from Zhao et al. [13] LEV-2 represents vehicles manufactured from 2004 to 2012. Fragments colored in blue represent aliphatic compounds, while those colored in orange are associated with aromatic compounds.

Figure 3. Comparison of IVOC volatility distributions of Chinses gasoline vehicle exhaust, US gasoline vehicle exhaust, and Chinses E10 fuel. The box-plot represents the Chinses gasoline vehicle exhaust. The boxes represent the 25th and 75th percentiles with the centerline being the median. The whiskers are the 10th and 90th percentiles. Red solid circles and blue hollow triangle represent IVOC fractions of US vehicle exhaust (Zhao et al., 2016) and Chinese E10 fuel in different volatility bins, respectively.

Figure 4. Comparison of emission factors of (a) PM (b) NO_x (c) THC, and (d) IVOC between China and US on road gasoline vehicles (Zhao et al., 2016;May et al.,

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

2014). The boxes present the 75th and 25th percentiles with the centerline represents being the median. The US vehicles are grouped by the model year, i.e. pre-LEV refers to vehicles manufactured prior to 1994, LEV-1 represents vehicles from 1994-2003, and LEV-2 is vehicles manufactured from 2004-2012.

Figure 5 Comparison of POA and estimated SOA production after 48 h of photo-oxidation (a) under low NO_x condition; (b) at an OA loading of 10 μg·m^{-3} under high NO_x condition; (c) at an OA loading of 20 μg·m^{-3} under high NO_x condition; (d) at an OA loading of 80 μg·m^{-3} under high NO_x condition.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

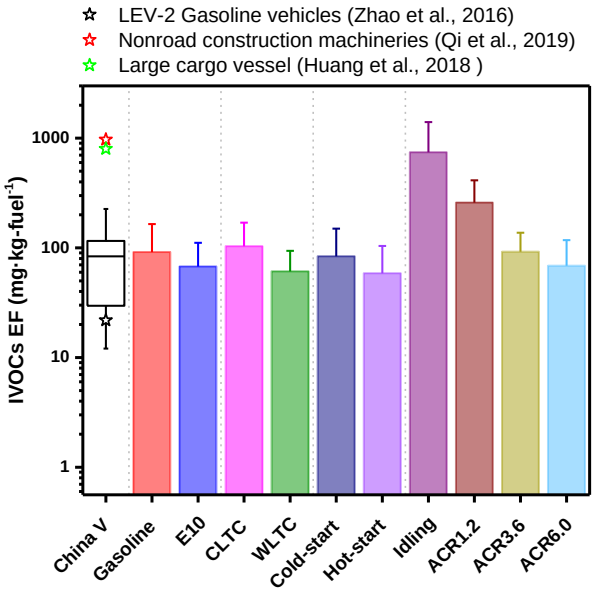

Figure 1. IVOC emission factors measured under different conditions, i.e. different fuel type (gasoline, E10), test cycles (Chinese Light vehicles Test Cycle, CLTC, and World-wide harmonized Light-duty Test Cycle, WLTC), starting mode (hot start and cold start), and acceleration rates (acceleration rates of 1.2, 3.6 and 6.0 km/h/s). Stars indicate the EF data from US, i.e. median US LEV-2 gasoline vehicles (vehicles manufactured in 2004-2012), non-road construction machinery, and a large cargo vessel (Qi et al., 2019;Huang et al., 2018;Zhao et al., 2016). The first category "China V" is the compilation of all the EF results from all of the CLTC and WLTC tests. The boxes indicate the median value, with error bars represent one standard deviation.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

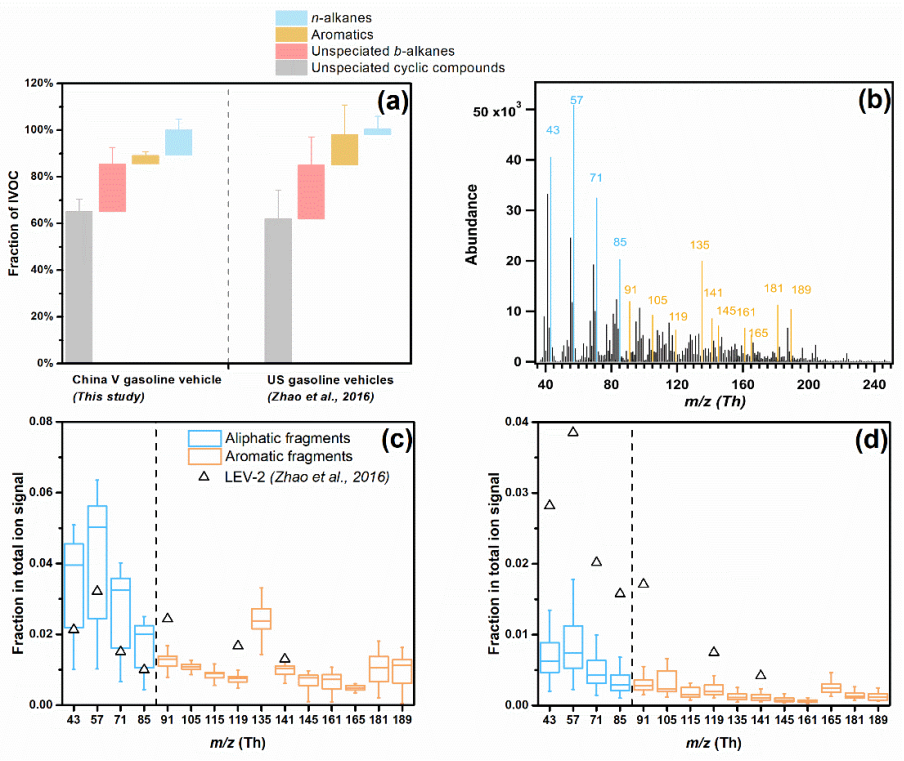

Figure 2. (a) Comparison of average chemical speciation of IVOC emissions from China V vehicle and US vehicles (Zhao et al., 2016); (b) Average mass spectrum of the IVOC during a typical E10-fueled cold start CLTC test. (c-d) Box-whisker plots of the fractional contribution of selected fragments to total IVOCs signal for tested China V vehicle：(c) B_{12}-B_{16} bins; (d) B_{17}-B_{22} bins. The boxes represent the 25th and 75th percentiles with the centerline being the median. The whiskers are the 10th and 90th percentiles. Black hollow triangles represent median LEV-2 data from Zhao et al. (2016) LEV-2 represents vehicles manufactured from 2004 to 2012. Fragments colored in blue represent aliphatic compounds, while those colored in orange are associated with aromatic compounds.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

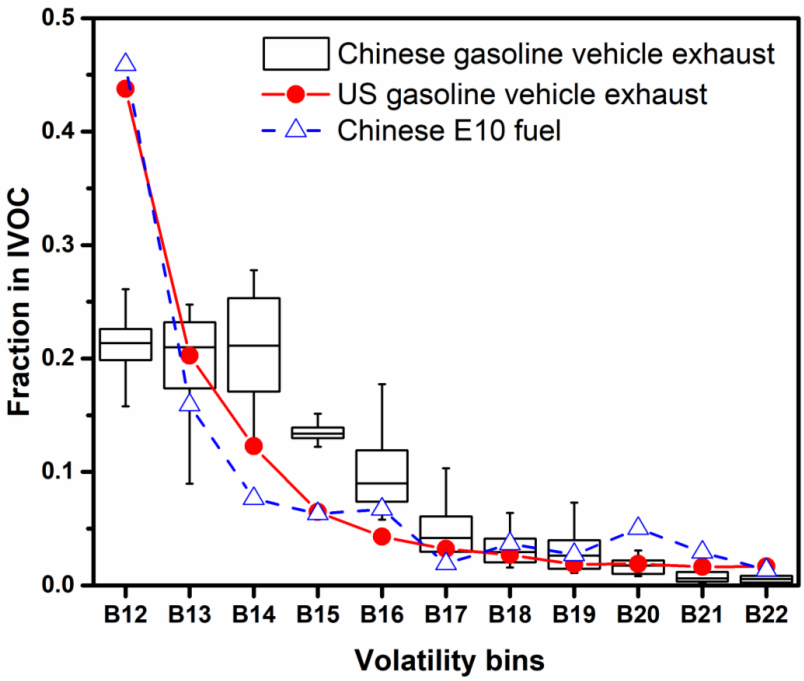

Figure 3. Comparison of IVOC volatility distributions of Chinses gasoline vehicle exhaust, US gasoline vehicle exhaust, and Chinses E10 fuel. The box-plot represents the Chinses gasoline vehicle exhaust. The boxes represent the 25th and 75th percentiles with the centerline being the median. The whiskers are the 10th and 90th percentiles. Red solid circles and blue hollow triangle represent IVOC fractions of US vehicle exhaust (Zhao et al., 2016) and Chinese E10 fuel in different volatility bins, respectively.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

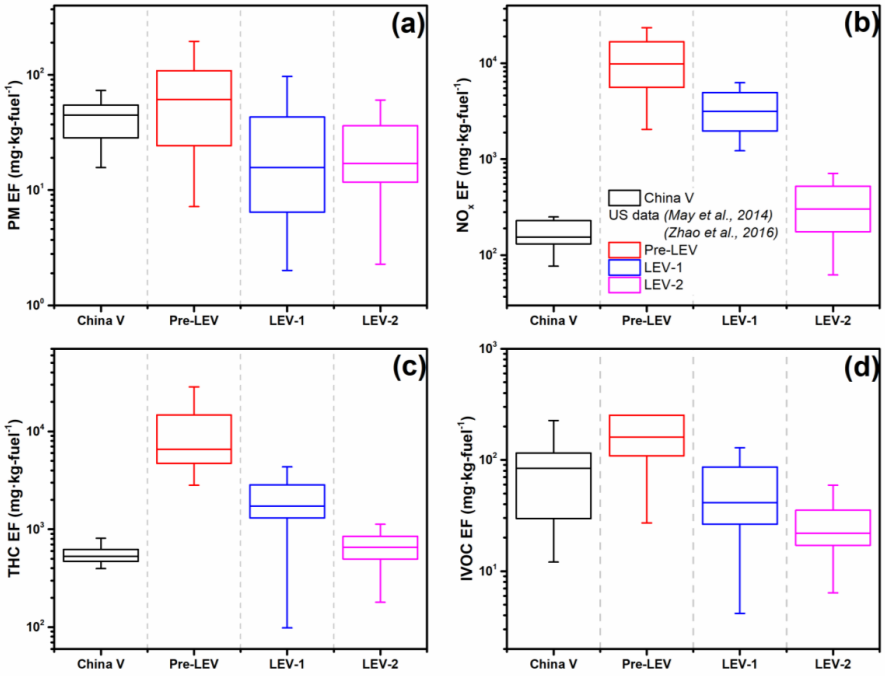

Figure 4. Comparison of emission factors of (a) PM (b) NO_x (c) THC, and (d) IVOC between China and US on road gasoline vehicles (Zhao et al., 2016;May et al., 2014). The boxes present the 75th and 25th percentiles with the centerline represents being the median. The US vehicles are grouped by the model year, i.e. pre-LEV refers to vehicles manufactured prior to 1994, LEV-1 represents vehicles from 1994-2003, and LEV-2 is vehicles manufactured from 2004-2012.

https://doi.org/10.5194/acp-2020-976
Preprint. Discussion started: 13 November 2020

Atmospheric Chemistry and Physics Discussions

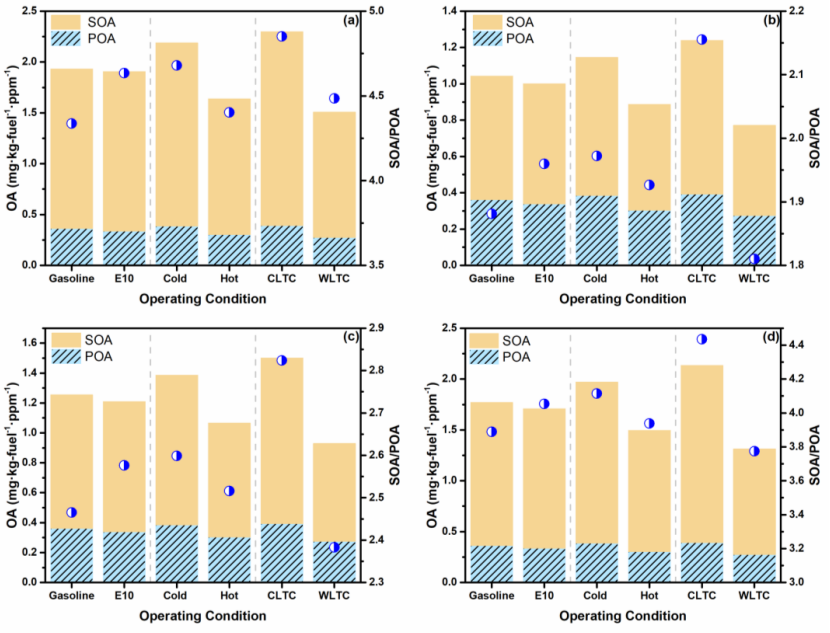

Figure 5 Comparison of POA and estimated SOA production after 48 h of photo-oxidation (a) under low NO_x condition; (b) at an OA loading of 10 μg·m^{-3} under high NO_x condition; (c) at an OA loading of 20 μg·m^{-3} under high NO_x condition; (d) at an OA loading of 80 μg·m^{-3} under high NO_x condition.