Secondary Organic Aerosol from On- and Off-Road Combustion Emissions: Scientific and Policy Perspectives

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I wish that my father could have seen me finish my degree. I think that he would have never guessed that I would be where I am today, but then neither would I.

Abstract

Combustion emissions from on-road sources such as light duty gasoline vehicles (LDGV), medium duty diesel vehicles (MDDV) and heavy duty diesel vehicles (HDDV) as well as small off-road engines (SORE) such those used in lawn and garden equipment are a major source of fine particulate matter (PM) pollution in the ambient atmosphere. Existing regulations have restricted direct PM emissions, especially for on-road sources; however, recent studies suggest that organic PM formed from the photo-oxidation of gaseous precursor emissions—so-called secondary organic aerosol (SOA)—contributes at least as much to the overall PM burden as PM "emitted from the tailpipe." A major limitation of many of these studies is that they attempt to induce from the behavior of simple emission surrogates (e.g., vaporized whole fuel) the behavior of actual combustion emissions from real world sources.

This research investigates combustion emissions directly. The primary gas- and particlephase emissions, SOA production and SOA yields from a range of different on-road and off-road combustion sources were characterized. LDGV, MDDV and HDDV were driven on chassis dynamometers over realistic, urban driving cycles. Off-road sources, including 2- and 4-stroke lawn and garden equipment and a diesel transportation refrigeration unit were tested using engine dynamometers operated over certification cycles.

For nearly all gasoline engines (LDGV and SOREs), photo-oxidizing dilute combustion emissions for 3 hours produced at least as much SOA as the directly emitted primary PM. SOA increased net PM production for LDGV by a factor of 1-10, depending on the vehicle emission standard. SOA yields were found to *increase* with newer vehicles, which have lower primary emissions. SOA for diesel vehicles, while still large on an absolute basis, was a smaller fraction of the primary PM emissions (between 10-30%), due to the very high elemental carbon (EC) emissions from vehicles without diesel particulate filters (DPF). Aftertreatment systems utilizing a DPF and a diesel oxidation catalyst essentially eliminated primary PM and SOA. Among the off-road sources, SOA from 2-stroke emissions increased the net PM by roughly a factor of 2.

Primary emission and SOA production factors from the various combustion sources tested in this work were combined with fuel consumption data for California's South Coast Air Basin (SoCAB) to determine the impact on the aggregate PM from on- and off-road sources in the region. These estimated impacts were compared to the PM values derived from the regulatory models EMFAC and OFFROAD. Our data indicate that PM from on-road gasoline sources is significantly under-represented by existing emissions models due to the dominant role of SOA. When SOA production is included, newer LDGV are one of the largest sources of PM in SoCAB. Furthermore, LDGV will become an even more important PM source once existing regulations requiring DPF retrofits on both on- and off-road diesel sources are implemented over the next few years. While on-road diesel vehicles are currently an important source of PM based on total fuel consumption, LDGV are responsible for a larger fraction of total PM. The primary and secondary PM contribution of off-road sources also appear to be high, but the magnitude remains highly uncertain, pending further experimental data. Evidence is presented that suggests that existing models may dramatically overpredict primary PM emissions from off-road sources.

Regulators are strongly urged to consider the impact of SOA on net PM production.

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List of Abbreviations

AMS	Quadrupole aerosol mass spectrometer
ARB	Air Resources Board
B100	"Neat" (100 percent) biodiesel
BC	Black Carbon
CARB	California Air Resources Board
CFR	Code of Federal Regulations
CMU	Carnegie Mellon University
СТМ	Chemical transport model
CO	Carbon monoxide
C _{oa}	Organic aerosol concentration
CVS	Constant volume sampler
DPF	Diesel particulate filter
DNPH	2,4-dinitrophenyl hydrazine
DOC	Diesel oxidation catalyst
EC	Elemental carbon
EF	Emission factor
EMFAC	CARB's Emission factor model (on-road)
FID	Flame ionization detector
FTP	Federal Test Procedure
GDI	Gasoline direct injection
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
НС	Hydrocarbons
HDDV	Heavy-duty diesel vehicle
HEPA	High efficiency particulate air
HONO	Nitrous acid
HSL	Haagen-Smit Laboratory
IVOC	Intermediate volatility organic compound
LDGV	Light-duty gasoline vehicle
LDT	Light-duty truck
LDV	Light-duty vehicle
LEV	Low emission vehicle
LEV-1	Low emission vehicle (model years 1994-2003)
LEV-2	Low emission vehicle (MY2004-current)
LVOC	Low volatile organic compound
MDDV	Medium-duty diesel vehicle

<i>m/z</i>	mass-to-charge ratio
NMHC	Non-methane hydrocarbons
NMOG	Non-methane organic gases
NOx	Oxides of nitrogen
OA	Organic aerosol
OC	Organic carbon
OFFROAD	Off-road emission model
OH	Hydroxyl radical
PAH	Polyaromatic hydrocarbon
PEMS	Portable emissions measurement system
PM	Particulate matter
POA	Primary organic aerosol
pre-LEV	pre-Low emission vehicle (model years before 1994)
PSI	Pounds per square inch
PTRMS	Proton transfer reaction mass spectrometer
QBT	Quartz behind Teflon filter
RVP	Reid vapor pressure
SCR	Selective catalytic reduction
SMPS	Scanning mobility particle sizer
SOA	Secondary organic aerosol
SoCAB	California's South Coast Air Basin
SOP	Standard operating procedure
SORE	Small off-road engine
SUV	Sport utility vehicle
SVOC	Semivolatile organic compound
TD-GC-MS	Thermal desorption gas chromatography mass spectrometry
TOG	Total organic gases
TRU	Transportation refrigeration unit
UC	Unified cycle (also known as 'LA-92')
UCM	Unresolved complex mixture
ULEV	Ultra low emission vehicle
ULSD	Ultra-low sulfur diesel
UDDS	Urban Dynamometer Driving Schedule
VBS	Volatility Basis Set
VOC	Volatile organic compound

Chapter 1: Introduction

1.1 Background: Origins and Impacts of Particulate Matter

One third of the U.S. population lives in areas where the concentration of airborne particulate matter (PM) exceeds the National Ambient Air Quality Standards. PM has significant adverse impacts on human health, including responsibility for an estimated 50,000 premature deaths annually in the United States [1-6]. Furthermore, PM reduces atmospheric visibility, and although the net impact remains highly uncertain, PM affects the Earth's radiative balance substantially through both direct and indirect effects [7-13].



Figure 1.1. Taxonomy illustrating the different classes of PM and PM precursors.

PM originates from natural sources such as windblown dust, volcanic eruptions and sea spray as well as from anthropogenic sources such as fossil fuel-fired power plants, biomass fuelfired cook stoves and internal combustion engines. PM can exist in either the solid or liquid phase and is referred to as primary PM when emitted directly "from the tailpipe." It is thus distinguished from secondary PM which refers to particulate matter formed in the atmosphere from the oxidation of gaseous precursor emissions. PM may be inorganic (including metals) or organic. Combustion-derived PM – especially that originating from internal combustion engines – deserves particular attention, as it represents a large source of anthropogenic emissions [14, 15], and a schematic taxonomy of this source is provided in Figure 1.1.

As noted by Robinson et al. recently [16], the chemical and physical processes governing the evolution of inorganic PM – both primary and secondary – have been investigated extensively; this research field is relatively mature. On the other hand, organic PM is less well understood, although previous research has unequivocally demonstrated that organics constitute a large (albeit inadequately constrained and spatially heterogeneous) fraction of the total fine PM (i.e., PM with diameters < 2.5 microns) in the atmosphere – contributing between 20-90% depending on location [17-21]. Furthermore, numerous reports have shown that the secondary fraction of fine organic PM (i.e., secondary organic aerosol, "SOA") dominates primary organics ("POA"), even in urban areas [19, 22, 23]. Zhang et al. surveyed ambient data from 37 sites – distributed in urban, urban downwind and rural locations across the globe – and found that OOA (oxidized organic aerosol, associated with SOA) accounted for a greater fraction of total OA than HOA (hydrocarbon-like organic aerosol, associated with POA). In the Zhang et al. study SOA (or OOA) comprised 63%, 83% and 95% of the total ambient OA burden for the urban, urban downwind and rural locations.

In addition to ambient atmospheric studies, numerous laboratory studies of different combustion systems have demonstrated that the mass of SOA generated from precursor gases can be at least as great as the mass of the POA. Weitkamp et al. photo-oxidized dilute diesel exhaust (Figure 1.2) and found that the amount of SOA generated after 3.5 hours was approximately equal to the POA [25]. Lee et al. reported nearly the same result with dilute diesel combustion emissions [26]. Grieshop et al. [27] found similarly high SOA levels from the emissions of a wood stove. Substantial but somewhat lower SOA yields – approximately 45% of total OA was attributed to SOA – were reported by Samy and Zielinsksa for photo-oxidized combustion emissions from a LDDV engine run on a dynamometer, but it is believed that these results represent a lower limit on published SOA yields to date for combustion systems under realistic conditions [28].



Figure 1.2. Wall-loss-corrected PM mass measured during photooxidation of diesel emissions [25]. Traditional SOA models may underpredict SOA by a factor of 3 or more.

The explanation for the unexpectedly large ratio of SOA to POA discovered in diesel exhaust, wood smoke and many other emission sources is still an active area of research. The amount of SOA generated by these sources far exceeds levels predicted by models parameterized by the SOA yields derived for precursor gases traditionally assumed to dominate SOA production (e.g., single-ring aromatics). For example, using the most up-to-date SOA yields, Robinson et al. were only able to explain 25% of the SOA from the photo-oxidation of dilute diesel exhaust [16]. Miracolo et al. showed that although the PM emissions from an aircraft operated at low (4%) engine load were dominated by SOA, an updated model was only able to predict 40% of the observed SOA [29]. Furthermore, many local, regional and global scale computer models systematically underpredict the measured ambient SOA [30-32]. This was especially true in models that only parameterized biogenic VOCs (assumed dominant at the global scale) and/or anthropogenic VOCs. In contrast to these early models, it has been proposed that lower volatility compounds – so-called semi- and intermediate-volatility organic compounds (SVOC and IVOC) – previously assumed to be non-volatile and non-reactive, may lead to SOA via two different pathways: (1) gas phase SVOC or IVOC emitted from the tailpipe may oxidize and form SOA or (2) primary PM (in the form of SVOC) may partition to the gas phase, oxidize and become less volatile and, finally, condense into solid or liquid particles (i.e., SOA) [33-35]. Models which incorporate this SOA production mechanism have been more successful in predicting observed SOA concentrations in the atmosphere [36-38].

The foregoing discussion presents evidence from the literature that (1) OA is a major contributor to harmful ambient-level PM emissions, (2) SOA concentrations often dominate POA and (3) oxidation of lower volatility (SVOC and IVOC) compounds may be an important, but largely unaccounted for source of SOA. From a public policy perspective items (1) and (2) lead ineluctably to the conclusion that considerable regulatory attention should be focused on SOA and its precursors. However, **there are currently no regulations which aim to reduce SOA precursor emissions directly**, despite the fact that in large nonattainment areas such as Los Angeles 70-90% of the organic aerosol is SOA [39], and a significant fraction of this SOA is due to precursor emissions from on- and off-road combustion sources. Thus, it seems likely

that much of the remaining benefit from air pollution policy in many urban nonattainment regions will probably come from regulations that limit SOA precursor emissions, and item (3) suggests a potential path forward: if lower volatility (SVOC and IVOC) compounds are in fact proven to be a key source of SOA, then efficient regulations should aim to reduce these precursors. But this approach diverges significantly from the strategy and methods traditionally employed by regulators to mitigate PM emissions.

1.2 Regulating PM: On- and Off-road Sources

To date the regulatory strategy has been to incrementally ratchet down primary PM limits. This is true both for on-road sources including gasoline- and diesel-powered cars, trucks and buses as well as for off-road sources, which comprise a very diverse category, including lawn and garden equipment (lawnmowers, leaf blowers), recreational vehicles (boats, ATVs) and construction equipment (bulldozers, generators), among others. For example, the California Air Resources Board (CARB) is currently considering tightening the existing 10 mg/mile LEV-2 light-duty vehicle (LDV) PM standard by implementing a 3 or even a 1 mg/mile LEV-3 standard.

On the one hand, reducing primary PM limits has been very effective in the past, and the increasingly stringent regulation of SO₂, NO_x, O₃, Pb, CO and primary PM stipulated by the Clean Air Act (CAA) amendments in 1970, 1977 and 1990 *have* profoundly improved air quality in the United States: from 1970-2008 the U.S. population increased 48%, VMT increased 163% and GDP increased 209%, while total criteria pollutant emissions decreased 60% and PM2.5 (PM2.5 has only been systematically measured since 1999) levels decreased 30% [40]. On the other hand, now that so much of the "low hanging fruit" has been picked and the primary

emissions from vehicles are radically cleaner than they were before the CAA, will the existing, primary PM-focused regulatory framework as prescribed in the Code of Federal Regulations continue to generate as large of a return on investment as it has over the last 40 years? Have we reached a tipping point beyond which additional significant ambient PM reductions will require either a modified regulatory approach or Draconian costs under the existing approach?

There are significant differences in on- and off-road combustion sources—both with respect to their engine and emission control technologies and the historical trajectory of the regulations governing them, and it is not clear that strategies for mitigating pollutants from on-road sources are the best ones to use for off-road sources. Regarding the policy trajectory for on-road sources, the earliest regulations with any teeth were established nationally (California began regulating on-road earlier than the EPA) with the 1970 Clean Air Act Amendments, which required a 90% reduction of tailpipe emissions from the then uncontrolled vehicles by the 1975 model year [41]. In contrast to on-road sources, the combustion emissions from both small (< 19 kW) off-road engines (SORE) as well as transportation refrigeration units (TRU, used to cool perishable cargo during transport) were not regulated in the US until 1995. These two off-road examples are representative of the lag in regulatory stringency between on- and off-road sources.

This lag notwithstanding, off-road sources have come under increasing regulatory scrutiny in recent years as their impact on air quality has become clearer. While responsible for only 1-2% of the fuel consumption of on-road vehicles [42, 43], some SORE—which include both 2-stroke configurations, typically used to power handheld equipment and 4-stroke configurations for non-handheld applications—are known to have high emissions of gas- and particle-phase pollutants [41].

While certain regulations (e.g., limits on the mass of total non-methane organic gases) have likely reduced emissions of SOA precursors, these blunt instruments have only inefficiently and partially achieved this end. This is because vehicles and off-road sources emit an array of different non-methane organic gases (NMOG), and these NMOGs will have varying SOA yields. For example, Odum et al. reported the SOA yields of 17 different aromatic species; the lowest yield was $\sim 2\%$ (o-xylene), while the highest yield was $\sim 12\%$ (ethylbenzene) [44]. This wide range in yields shows that NMOGs are not equally important from the perspective of SOA production; therefore, regulating all NMOGs equally will not necessarily be the most efficient method of limiting SOA. In fact, the vast majority of NMOGs are not SOA precursors because only those species with about 6 carbons or more are of low enough volatility to produce SOA. Although the practicality of wide-scale implementation has not yet been evaluated, much greater benefits could theoretically be derived by regulating vehicles' emissions based on their SOA formation potential. A possible model for such a strategy- the maximum incremental reactivity (MIR) scale – was implemented in 1993 by CARB to address the variability of ozone yields from different VOCs [45, 46].

1.3 PM Mitigation: The Role of Fuel Chemistry

The MIR scale was the product of experimental studies dating from the early 1970s to develop methods for modifying combustion emissions through the systematic modification of fuel properties. These early studies, reviewed by Koehl et al., as well as a major series of studies in the 1990s, the Auto/Oil Air Quality Improvement Research Program (AQIRP), quantified the relationship between gasoline composition and emissions [47]. In so doing, this work supported the development of reformulated gasoline (RFG), which was required by the 1990 CAA

amendments to be used in the nine most seriously polluting cities in the U.S. by 1995 (although it was introduced in some areas as early as January 1992). The California phase 1 RFG set limits on Reid Vapor pressure, oxygen content, benzene, total aromatics and other fuel properties. In addition to reducing ozone, these modifications reduced NOx, CO and air toxics [48]. Following the phase 1 RFG, fuel properties were further restricted by the CA transitional RFG (introduced January 1995) and then by the CA phase 2 RFG (introduced in the first half of 1996) [49].

While phase 1 RFG appears to have been an unqualified success in reducing ozone, CO and air toxics, the marginal benefit from phase 2 RFG is somewhat less clear. On the one hand, in a series of experiments conducted between 1994 and 1997 in San Francisco's Caldecott tunnel, Kirchstetter et al. concluded that since phase 2 RFG reduced VOC emissions by 40% (but NOx reductions were much less), it would be an effective ozone-reducing strategy in areas that are VOC-limited [49]. On the other hand, Gertler et al., in an independent series of experiments in Los Angeles's Sepulveda tunnel, found that after accounting for the reactivity (via the MIRweighting) of the speciated NMOG emissions, the ozone forming potential was not significantly different before and after the introduction of phase 2 RFG [50].

One of the important lessons to be drawn from these fuel reformulation efforts is that changes to fuel composition can be deployed much more quickly than modifications to engine or aftertreatment technologies. It can take many years for engine or emission control technologies to diffuse through to a significant percentage of the vehicle and off-road fleet—even if retrofit campaigns are undertaken. However, past experience with phase 1 and 2 RFG have shown that diffusion of a new fuel formulation throughout the fleet can happen much more rapidly.

While SOA was not a major consideration in the development or implementation of RFG (ozone reduction was), strong parallels exist between the formation of ozone and SOA. Like

ozone, SOA is formed from the photo-oxidation of organic gases, but unlike ozone, viable SOA precursors are generally restricted to the less volatile organic compounds (C_7 or greater), whereas reactivity that strongly influences O_3 is dominated by more volatile compounds (C_7 and smaller).

Odum et al. investigated whether fuel reformulation might also be effective in reducing SOA. They determined the SOA yields from the whole gasoline vapors from 12 different reformulated gasolines provided by the Auto/Oil Air Quality Improvement Research Program (AQIRP), which was one of the major research consortia developing RFG [44, 51]. They also determined the individual SOA yields of 28 of the 57 speciated aromatics in phase 2 RFG (which accounted for 95% of the total aromatic mass of the fuel). By knowing the amount of each of the aromatic species that reacted during the photo-oxidation of a particular gasoline formulation, they were able to predict the SOA yield of this formulation. Strikingly, when plotted against the measured SOA yields from whole gasoline vapor (see Figure 1.3), the predicted yields fell on a line with slope of 1.00±0.16, indicating near perfect agreement between measured and predicted SOA yields for the 12 different gasoline formulations tested.



Figure 1.3. Comparison of measured SOA yields from 12 different reformulated gasolines and the SOA yields predicted from the amount of SOA generated solely by the aromatic content of the fuels. Letters refer to different fuel formulations. From [51].

If whole gasoline vapor were an accurate and complete surrogate for *combustion* emissions, then the problem of how to reformulate fuel to reduce SOA would have been largely solved by Odum et al. However, as described previously, it has been shown repeatedly that traditional VOC-based SOA models (for which aromatics are the dominant SOA precursors) systematically underpredict SOA from a variety of sources, thereby casting serious doubt on the adequacy of using whole gasoline vapor as a combustion emissions surrogate. While whole vapor experiments may be indicative of general trends of SOA yields from vehicle combustion emissions, it will clearly be beneficial to measure yields from combustion emissions directly.

In addition to modifying fuel properties, PM reduction may also be achieved by instituting a wholesale change in fuel composition to non-petroleum alternatives such as biodiesel. Although the primary impetuses for this approach are increased sustainability and energy independence, many studies show that changing from petroleum diesel to biodiesel (BD) also reduces carbon monoxide, hydrocarbons and primary PM [52]. To my knowledge there has been no work done to examine the effect of fuel reformulation/additives on the SOA yields of combustion emissions. There appear to be, for example, no studies investigating the SOA yields of biodiesel combustion emissions.

1.4 PM Mitigation: Role of Aftertreatment Technologies

Until recent and relatively stringent changes to national emissions standards in 2007 and 2010 effectively mandated aftertreatment (AT) technology for heavy duty diesel vehicles (HDDV), progress in reducing emissions from HDDV has been slower than with LDV (although HDDV limits are (and were) still more stringent than for off-road sources). Furthermore, it has been estimated that although HDDVs account for only 2% of the U.S. on-road vehicle fleet and

4% of the VMT, they are responsible for over half of the PM and NOx from all motor vehicles; this is largely due to the successes in controlling LDV emissions coupled with a consumption growth rate that is 3x greater for diesel than for gasoline [53]. In light of these facts, it is critical to investigate HDDVs with and without AT in order to render a more complete picture of the landscape of on-road emissions.

While numerous studies have demonstrated the effectiveness of specific aftertreatment devices such as diesel particulate filters (DPFs) in reducing primary PM [54], diesel oxidation catalysts (DOCs) in reducing CO and volatile organics (and to a lesser extent, primary PM) [55] and, selective catalytic reduction (SCR) and lean NOx catalysts (LNCs) in reducing NOx [56], the only study that has explored the impact of aftertreatment on SOA is the recent one by Chirico et al. [57]. With the dramatic reduction (>95%) in primary PM emissions achievable with DPFs, the relative importance of SOA might be expected to increase correspondingly since the precursor gases are not trapped by DPFs. However, it is becoming increasingly common to find multi-functional aftertreatment devices which package DPF, DOC and/or LNC in a single substrate [58], and catalyzed DPFs or DOCs are quite effective in reducing some fraction of the organic emissions (e.g., aromatics, carbonyls, PAHs) [59] which could lead to the formation of SOA. Thus, Chirico et al. found (Figure 1.4) that a diesel oxidation catalyst significantly reduced the SOA formed from the emissions of light duty vehicles [57], while the DPF virtually eliminated POA and BC. There are, to my knowledge, no similar studies with heavy duty diesel vehicles.



Figure 1.4. Impact of aftertreatment on several light duty diesel vehicles. Fuel-based emission factors for six different vehicle and AT scenarios. Key: no AT=no aftertreatment; DOC deact., warm=non-functioning diesel oxidation catalyst, measured after warming up engine; DOC act.=functioning DOC. From [57].

1.5 Outline of Dissertation

The fundamental goal of this dissertation is to increase our understanding of secondary organic aerosol formed from the combustion emissions from both on- and off-road sources. Subsequent chapters describe the results of our efforts to do so.

Chapter 2 addresses the first objective of this research, which is to characterize SOA production from the emissions of gasoline cars and light trucks. This chapter presents the largest set of results in the dissertation. It describes experiments with 64 different gasoline vehicles, including both primary gas- and particle-phase measurements as well as SOA production in smog chamber experiments. The vehicles used in the smog chamber studies spanned a range of types, model years and emission standards. Collectively, they constitute a representative sampling of the existing gasoline vehicle fleet. From such a large and varied sample we are able to draw robust conclusions about the magnitude of SOA production from this

important PM source. Chapter 2 also introduces many of the experimental and data analysis methods used in subsequent chapters. For example, the method used to calculate SOA yields is described in this chapter in detail. This approach is then used in Chapter 3 to calculate SOA yields for diesel vehicles (and will be used for the experiments in Chapter 4 once the necessary data are provided by CARB), although it is modified slightly to account for the different types of data reported for the different sources.

The next objective, addressed in **Chapter 3**, is to investigate SOA production from the emissions of medium- and heavy-duty diesel vehicles (MDDV and HDDV). Unlike the studies with cars and light trucks in Chapter 2, which used a single fuel in all experiments, Chapter 3 investigates whether or not changing the chemical composition of the fuel used with these vehicles is a viable approach to mitigating PM—both primary and secondary. In addition, the vehicles tested in Chapter 3 span a wide range of emission control systems, including those with no aftertreatment (e.g., diesel particulate filter, DPF) and those with the current state of the art emission controls. We also quantify the impact of different driving cycles on primary and secondary PM. Finally, the SOA yields for diesel vehicles are calculated and compared to gasoline vehicles.

Chapter 4 focuses on the third major objective: to investigate PM from off-road sources. In this chapter we describe the results from an experimental study of primary and secondary PM derived from seven different small off-road engines (SORE, gasoline-fueled) and a diesel-fueled transportation and refrigeration unit (TRU) used to cool perishable cargo during truck transport. Our data characterize only a small subset of the diverse range of off-road engines, but these data are, nevertheless, some of the first describing the SOA production from this large combustion source category.

The objective of **Chapter 5** is to put the experimental work from this dissertation in context by shifting the focus from the emissions and SOA production of individual sources to a more holistic picture of PM pollution from all on- and off-road combustion sources that may be useful to policymakers. First, the experimental results of the preceding three chapters are summarized and both the primary emissions and SOA production from the different on- and off-road sources are compared to one another to assess their relative impact per mass of fuel consumed. Then, fuel consumption data is obtained for on- and off-road sources in the South Coast Air Basin (of southern California) from two different emissions/fuel consumption models developed by CARB. The fuel consumption data are combined with the experimentally-derived primary PM emission factors and SOA production factors to estimate the regional contribution of emissions from these sources to fine PM.

Finally, in **Chapter 6** I suggest several directions for future work that could build on the efforts presented in this dissertation.

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Chapter 2: Secondary Organic Aerosol Formed from Gasoline Powered Light Duty Vehicle Exhaust Dominates Primary Particulate Matter Emissions

2.1 Abstract

The effects of photochemical aging on particulate matter emissions from 15 light duty gasoline vehicles (LDGV) were investigated to probe the critical link between tailpipe and the ambient atmosphere. The vehicles were recruited from the California in-use fleet. For every vehicle, substantial secondary organic aerosol (SOA) formation was observed—with the emissions from some vehicles generating as much as 6 times the amount of SOA as primary particulate matter after three hours of oxidation at typical atmospheric oxidant levels. The aerosol mass spectrometer shows that the SOA in the smog chamber oxidizes rapidly, transforming into lower volatility, oxygenated species typical of the ambient atmosphere. The mass of SOA generated by photo-oxidizing exhaust from newer vehicles was comparable to that from older vehicles, despite large differences in primary emission rates. The absolute amount of known SOA precursor emissions have decreased substantially with newer vehicles; thus, the speciated HCs alone do not explain the difference in SOA yields for different vehicles.

2.2 Introduction

Particulate matter (PM) is commonly classified as either primary or secondary. Primary PM is emitted directly "from the tailpipe"; secondary PM is formed in the atmosphere from the oxidation of gaseous precursor emissions. Combustion-derived PM (both primary and secondary)—especially that originating from emissions from internal combustion engines—deserves particular attention, as it represents a large source of anthropogenic emissions [1, 2].

Although organic aerosols are a major component of atmospheric PM2.5, its sources are poorly understood [3, 4]. Furthermore, numerous reports have shown that the secondary fraction of fine organic PM (secondary organic aerosol, SOA) dominates primary organic aerosol (POA), even in urban areas with substantial fresh POA emissions [5-7]. However, chemical transport models systematically underpredict SOA levels [8-10], especially in photochemical episodes [11], thereby significantly limiting their utility in defining effective PM control strategies.

To date mobile source emissions regulations have focused on incrementally reducing primary PM2.5 emissions from motor vehicles, but it is ultimately the net (primary + secondary) contribution of these emissions to ambient PM2.5—which may peak far downstream from vehicles' tailpipes due to secondary PM production—that is responsible for the array of deleterious human health and environmental impacts. While mandated reductions of emissions of total non-methane organic gases (NMOGs) have reduced emissions of SOA precursors, these policy instruments may only partially achieve this end because vehicles emit hundreds or thousands of different NMOGs, many of which are too volatile to form SOA [12, 13].

Recent laboratory studies of different combustion systems, including diesel generators, medium- and heavy-duty diesel vehicles, biomass burning and jet aircraft [14-19], have

demonstrated that the mass of SOA generated from the oxidation of vapor emissions often exceeds the mass of the POA. Therefore, secondary PM production from gaseous precursors represents a significant fraction of the atmospheric PM from these sources. Although much is known about primary PM emissions from light duty vehicles (LDVs), there are, to our knowledge, no published reports on SOA formation from gasoline-powered LDV. While diesel vehicles often have higher emissions than the historically more heavily regulated gasoline vehicles, gasoline-powered LDVs (e.g., passenger cars, light trucks and SUVs) are responsible for the vast majority of vehicle miles traveled and fuel consumed by on-highway vehicles; therefore, it is not so clear which type of vehicle is responsible for the greater share of the atmospheric PM burden—especially since an accurate assessment depends on the formation of SOA as well as direct emissions of POA and inorganic PM.

This study investigates SOA formation from 15 light duty gasoline vehicles recruited from the California in-use fleet. The vehicles span a range of types, model years and emission standards, and they were operated over a realistic driving cycle. Dilute emissions were injected into a smog chamber and then photo-oxidized to characterize secondary PM formation.

2.3 Materials and Methods

2.3.1 Experimental Setup

Emission characterization and photochemical aging experiments were conducted at the California Air Resources Board's (CARB) Haagen-Smit Laboratory in El Monte, California. A schematic of the test set-up is shown in Figure 2.2. Detailed descriptions of these facilities have been published previously [20]. The focus of this report is the results from 29 smog chamber experiments, but extensive additional primary only tests were performed with these vehicles and are described in a forthcoming paper [21].

Sixty-four light duty gasoline vehicles (LDGV) were recruited from the California in-use fleet for primary emissions testing and 15 of these vehicles were also tested using the smog chamber (see Table 2.3 for a detailed description of the smog chamber test vehicles and the initial conditions in all 29 chamber experiments). All vehicles tested in the chamber were operated on the same CA summertime commercial gasoline; details of its composition are provided in Table 4.2 below and Table 2.4 in the SI. We did not attempt to control for the greater wear and tear on older vehicles (although mileage and other indicators of use did not correlate with vehicle age in all cases).

Table 2.1. Fuel analysis of gasoline used in all LDGV experiments. The method of analysis and the relevant ASTM are also provided. Further compositional analysis and an elemental mass balance are provided in Table 2.4 of the SI.

MTBE (wt%)	oxygen (mass%)	benzene (vol%)	aromatics (vol%)	olefins (vol%)	olefins/ naphthalenes (mass%)	poly- naphthalenes (mass%)	RVP (psi)	T ₁₀ (°F) T ₅₀ (°F) T ₉₀ (°F)			sulfur (ppm)	density (g/ml)	
ASTM 4815, GC/FID		ASTM GC	D5580, :/FID	ASTM 6550 SFC			ASTM D5191		ASTM D80	5	ASTM 5453 ANTEK	ASTM D4052	
6.08	2.11	0.56	23.8	5.20	12.38	0.08	6.8	135	212	313	8.80	0.7410	

The vehicles were driven on a Clayton (Model AC-48) 48" single roll electric chassis dynamometer, and most experiments used the cold start Unified Cycle (UC) driving schedule (details shown in Figure 2.1). The UC has three phases (bags) and a soak period: Bag 1 is a 1.2 mile cold start phase lasting 300 seconds; Bag 2 is a 8.6 mile trip phase lasting 1135 seconds; these are run consecutively and followed by a 600 second hot soak (engine off); Bag 3 is a hot start phase and duplicates the specifications of Bag 1. Four hot start UC tests were also run (one pre-LEV, one LEV-1 and two LEV-2 experiments) to investigate the importance of the cold start phase on vehicle emissions. In the hot start experiments the vehicle was warmed up (emissions

were not sampled) using the Bag 1 portion of the cycle; immediately after finishing the warm-up the vehicle was driven according to the normal UC.



Figure 2.1. All vehicles were operated on a chassis dynamometer according to the Unified Cycle (UC), which consists of three phases, simulating urban stop-and-go driving conditions.

The UC is a more aggressive driving cycle than the federal FTP-75, featuring higher speeds, higher accelerations, fewer stops per mile, and less idle time. Emissions from vehicles operated over the UC are generally higher then when operated over the FTP—a cycle that has also been used in emission regulations. The two cycles are compared in Table 2.5 of the SI.

Tail pipe emissions were sampled using a Horiba constant volume sampling (CVS) system. Primary PM measurements were made by drawing a sample from the CVS through a pre-baked (to remove adsorbed carbonaceous contamination) 47 mm quartz filter and a combined Teflon filter + quartz filter (to correct for sampling artifacts) at 47°C following procedures described in CFR 1065 [22]. In brief, the pre-fired quartz-fiber filters were collected

and analyzed with a Sunset Laboratory Organic Carbon/Elemental Carbon (OC/EC) Analyzer using the IMPROVE protocol [23].



For the chamber experiments emissions were transferred from the end of the CVS via electrically heated (47 °C) 0.5" O.D. Silcosteel (i.e., passivated internal bore) tubing to a 7 m³ Teflon smog chamber where they were photochemically aged [18]. Before each experiment the chamber was cleaned by flushing with HEPA- and activated carbon-filtered air overnight. The chamber was clean before each experiment: less than 10 particles per cm³, NOx concentration <5 ppb. For experiments with low black carbon concentrations (listed in Table 2.3) the chamber was seeded to mitigate nucleation; approximately 10 μ g/m³ ammonium sulfate was injected into

Figure 2.2. Test set-up used for characterizing the photo-oxidized motor vehicle emissions (not to scale).

the chamber just before the vehicle was started. The smog chamber was located indoors, in a large air conditioned space; its temperature and humidity varied between 25°C-30°C and 30%-50%.

Vehicle emissions were added to the approximately half-filled chamber over the 38 minute UC (but not during the 10 minute hot soak period); thus, these experiments represent trip

average emissions. The chamber was covered (dark) during filling to prevent photo-chemistry. The exhaust inside the chamber was diluted by a factor of 200-300 compared to the tailpipe in three stages: first, it was diluted approximately 10:1 with ambient temperature HEPA-filtered air in the CVS; it was then diluted another 8-10:1 with 47°C HEPA- and activated carbon-filtered air using Dekati ejector diluters in the transfer line; finally, it was diluted another 2-3:1 in the smog chamber. After filling, PM concentrations inside the chamber were within the range of urban ambient conditions (~0.5 - 15 μ g m⁻³) for all of the vehicles. The mixing ratios of individual VOCs were typically less than 1 ppb, but were as high as 20 ppb for the highest emitting vehicle. NOx concentrations after injecting emissions were between 0.1 and 2.4 ppm.

After adding exhaust, HONO was introduced into the chamber as an OH radical source by bubbling dry air into a 1:2 solution (volume) of $0.1M \text{ NaNO}_2$ and $0.05 \text{ M H}_2\text{SO}_4$ for ~30 minutes and forcing the resulting gaseous mixture into the chamber. VOC/NOx ratios were adjusted to approximately 3:1 (typical of many urban environments) by adding propene (0.0-1.00 ppm), which is not considered to be a SOA precursor [16]. One high NOx experiment (VOC/NOx = 0.25) was also performed to investigate the impact of this parameter on SOA formation. After ~45 minutes of characterization of the primary emissions in the dark, the emissions were photo-oxidized by exposing them to UV lights (Model F40BL UVA, General Electric) continuously for 3 hours.

2.3.2 SOA Precursor Measurements

An important objective of this work is to better characterize the precursors that lead to SOA formation. In order to do this we obtained a comprehensive set of organic gas measurements from the CVS.

The measured gas-phase organics are grouped into eight different categories in Table 2.2. Collectively, five of the eight groups quantify concentrations of 203 individually speciated compounds (groups 2-6 in Table 2.2). Group 7 included both speciated data and a co-eluting set of compounds referred to as an unidentified complex mixture (UCM), but for this study these two subcategories within group 7 are lumped together. The FID measurement of THC in group 1 is assumed to include all gas-phase organics except IVOCs and SVOCs, since the latter are higher molecular weight and partition to the particle phase (where they are not seen by the GC-MS) more readily. Group 8 was defined by subtracting from group 1 all speciated and lumped compounds that were assumed to be measured by the FID (i.e., groups 2-6).

Samples from the CVS were collected in heated Tedlar bags and analyzed offline by CARB personnel for total hydrocarbons, methane, light hydrocarbons ($<C_5$), mid-weight hydrocarbons (C_5 to C_{12}) and carbonyls, using standard analytical procedures [24-26]. Briefly, concentrations of speciated C_2 to C_{12} hydrocarbons were determined from two gas chromatographs (GCs): one for analyzing the light-end (C_2 to C_5) hydrocarbons and the second for analyzing the mid-range (C_6 to C_{12}) hydrocarbons. The GCs were equipped with cryogenic pre-concentration (cryotrap) and automated, gas phase sampling valve systems. The light-end GC uses a Varian Al₂O₃/KCl porous layer open tubular (PLOT) analytical column [50 m x 0.32 mm inner diameter (ID)] to separate the hydrocarbon mixture. The mid-range GC uses a Varian DB-1TM analytical column (60 m x 0.32 mm ID, 1 um film thickness). Flame ionization detectors (FID) are used for hydrocarbon detection and quantification. The FIDs are calibrated with a NIST-traceable propane standard.

Low volatility organics in the diluted exhaust were collected using two parallel sample trains of a quartz filter (47 mm, Pall-Gelman, Tissuquartz 2500 QAOUP) followed by two

sorbent tubes (Gerstel 6mm OD/4.5mm ID glass tubes filled with 290 mg of a granular porous type of polymer, 2,6-Diphenyl p-phenyleneoxide, called TenaxTM TA) in series. The inlet line and sample box (filter and sorbent tubes) were maintained at 47°C. The flow rate through each quartz filter was 9.9 liter min⁻¹ and the flow rate through the sorbent tubes was 300 ml min⁻¹. A bypass line was used to exhaust the excess flow downstream of the quartz filter.

Filter and sorbent tube samples were analyzed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). This analysis is described in detail elsewhere[21]; we only briefly outline the method here. The Tenax[™] TA sorbent tubes were cleaned and conditioned via thermal desorption at 320°C under a constant 50 mL/min flow of ultrahigh purity helium. The thermal desorption unit was a Gerstel® TDS3 (Baltimore, MD) system mounted to the inlet of an Agilent 6890 GC and coupled to a mass spectrometer (Agilent 5975 MSD).

Concentrations of individual organic compounds in the quartz filter and TenaxTM TA sorbent samples were determined using multipoint calibration curves developed using authentic standards for a suite of target compounds and a deuterated internal standard to track analyte recovery. The emissions of 62 individual low-volatility organic compounds were quantified, including C_{12} and larger n-alkanes, cyclo- and branched alkanes, naphthalene, substituted naphthalenes, 3-ring polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes. Only a small portion (2.5%) of the total response from quartz filters and TenaxTM sorbent tubes was speciated. The majority of the chromatograms UCM and is not separable with traditional GC techniques. The mass of IVOC for each experiment was determined by multiplying the background-corrected OC (measured with the OC/EC analyzer) by the ratio of IVOC/SVOC, as determined by the TD-GC-MS.

Table 2.2. Eight different classes of organic gas-phase compounds characterized from the CVS. The number/type of compounds is reported as well as the laboratory techniques used to acquire and quantify the gases.

<u>group</u>	species in group	<u># species</u>	sampling method	method of quantification
1	total hydrocarbons		heated Tedlar bags	heated FID
2	methane	1	heated Tedlar bags	heated FID
3	low MW VOCs (speciated)	25	Tedlar bag	GC-MS with a Varian Al ₂ O ₃ /KCl PLOT column
4	mid MW VOCs (speciated)	164	Tedlar bag	GC-MS with a Varian DB- 1™ column
5	low MW carbonyls	11	DNPH cartridges	HPLC with a UV detector
6	aromatic carbonyls	2	DNPH cartridges	HPLC with a UV detector
7	S/IVOCs	lumped group	Quartz filter, Tenax tube	TD-GC-MS
8	NMOG balance	lumped group	n/a	$group_1 - \sum_{i=2}^{6} group_i$
Total spe	ciated compounds	203		

	test date	CARB test ID	expt ID	model year	vehicle class	engine size (L)	emission standard	mileage	UC driving cycle	VOC/ NOx	seed	mpg	SMPS PM @ t=0 hr (µg/m ³)	POA (µg/m³)	BC (μg/m³)	∆CO₂ (ppm)	NO (ppb)	NO ₂ (ppb)	d- butanol (ppm)	propene (ppm)	NMOG (ppmC)
Pre-LEV	2/14/12	1032442	PreLEV-1.1	1987	PC	4.1	Tierl	197,631	Cold	3.32	N	14.6	1.6	2.0	2.7	99	1095	0	0.06	0.13	1.82
	2/10/12	1032440	PreLEV-2.1	1088	DC	1.6	Tier I	224 758	Cold	4.31	N	24.1	4.4	9.2	5.7	206	1558	0	0.06	0.00	8.20
	2/13/12	1032444	PreLEV-2.2	1500	10			224,730	Cold	4.62	N	23.8	1.6	3.9	2.4	99	1095	0	0.06	0.00	3.20
	1/31/12	1032303	PreLEV-3.2		M3	5.0	Tier I	58,617	Cold	3.03	Y	13.1	3.6	22.7	0.8	452	1558	0	0.06	1.00	n/a
	2/1/12	1032389	PreLEV-3.3	1990					Cold	3.02	Y	12.9	15.4	19.0	0.8	407	1375	0	0.06	0.80	2.61
	2/8/12	1032426	PreLEV-3.4						Hot	3.08	Y	13.1	8.1	0.0	0.8	422.6	1117	0	0.06	0.60	2.91
	5/26/10	1027859	LEV1-1.5	1996	PC	2.7	Tier I	51,826	Cold	3.80	N	20.4	0.1	0.3	0.3	335.4	456	0	0.00	0.50	0.31
	1/17/12	1032302	LEV1-2.1		РС	3.0	LEV	130,485	Cold	3.17	Y	19.3	4.6	0.8	0.7	318	9	651	0.06	0.67	2.00
LEV I	1/18/12	1032304	LEV1-2.2	1997					Cold	3.91	Y	19.2	2.0	0.5	0.9	244.6	203	68	0.12	0.20	0.97
	2/15/12	1032473	LEV1-2.3						Hot	3.12	Y	19.1	2.6	0.5	0.7	264.0	183	76	0.06	0.27	1.06
	1/25/12	1032346	LEV1-3.2	1009	PC	3.0	LEV	90,638	Cold	3.16	Y	18.8	8.5	1.1	0.7	287.9	690	149	0.06	0.73	1.81
	1/26/12	1032362	LEV1-3.4	1998	FC				Cold	3.20	Y	18.3	7.1	0.9	0.5	268.9	364	50	0.06	0.33	1.36
	2/6/12	1032393	LEV1-4.1	1999	PC	2.0	TLEV	118,294	Cold	2.93	Y	23.6	12.5	0.8	0.6	234.5	400	32	0.06	0.53	1.24
	6/3/10	1027904	LEV1-5.2	2000	PC	2.2	LEV I, ULEV	104,446	Cold	3.37	N	23.0	1.0	2.7	0.5	251.9	170	182	0.00	0.35	0.15
	5/28/10	1027881	LEV1-6.1			3.5	LEV I, NLEV		Cold	3.48	N	17.1	7.1	0.9	8.3	118.6	1149	218	0.00	0.75	2.63
	6/1/10	1027917	LEV1-6.2	2003	PC			110,445	Cold	3.47	N	16.5	15.9	2.4	5.4	107.6	855	172	0.00	0.70	1.75
	6/2/10	1027918	LEV1-6.3						Cold	0.25	N	18.3	5.4	0.4	3.2	91.0	1570	0	0.00	0.00	1.73
	5/27/10	1027865	LEV2-1.2	2007	N/2	3.9	LEV II	29,433	Cold	3.43	N	16.6	2.0	0.7	3.6	416.1	93	221	0.00	0.25	0.16
	6/9/10	1027967	LEV2-1.6	2007	1013				Cold	3.28	N	16.4	7.6	0.6	4.9	316.7	61	168	0.00	0.20	0.12
	6/15/10	1028022	LEV2-2.1	2008	LDT	4.2	LEV II	43,378	Cold	4.18	N	15.4	9.4	0.6	7.9	388.2	83	119	0.00	0.25	0.14
	1/12/12	1032268	LEV2-3.1				LEV II	35,786	Cold	3.24	Y	19.7	1.0	0.4	1.7	165.3	138	74	0.06	0.13	0.82
_	1/13/12	1032283	LEV2-3.2	2008	PC	3.5			Cold	3.31	Y	19.6	1.2	0.7	3.1	162.4	220	155	0.06	0.51	1.60
	1/27/12	1032360	LEV2-3.3	2000					Hot	2.97	Y	20.4	9.1	0.6	4.0	265.5	146	144	0.06	0.20	0.80
ΓEΛ	1/30/12	1032359	LEV2-3.4						Hot	3.23	Y	21.3	16.6	1.0	4.6	289.6	137	174	0.06	0.27	0.80
	6/10/10	1027971	LEV2-4.2	2010	T2	3.6	ULEV; Tier II	18,236	Cold	4.06	N	15.8	14.8	0.8	11.4	335.5	23	166	0.06	0.06	0.59
	1/23/12	1032342	LEV2-5.1	2011	PC	2.0	LILEV/	10,911	Cold	3.12	Y	21.1	4.7	0.7	4.9	223.8	301	267	0.06	0.60	0.89
	1/24/12	1032351	LEV2-5.2	2011	10	2.0	OLEV		Cold	3.19	Y	22.3	7.9	0.9	6.2	237.5	304	268	0.06	0.47	1.20
	1/19/12	1032309	LEV2-6.2	2011	PC	26	LEV II, ULEV	29,249	Cold	3.29	Y	15.8	2.3	0.6	0.4	314.9	96	117	0.06	0.13	1.92
	1/20/12	1032321	LEV2-6.3	2011	PC	5.0			Cold	3.29	Y	15.9	4.7	0.6	0.5	298.3	9	239	0.06	0.13	0.66

Table 2.3. Specifications of all 15 different vehicles tested in the chamber are found in the left half of the table. Gas- and particle-phase concentrations in the chamber at t=0 h and other key experimental conditions for all 29 chamber experiments are found in the right half. Most vehicles were tested more than once.

A suite of instruments was used to characterize gas- and particulate-phase pollutants inside the chamber. Particle number distributions were measured with a scanning mobility particle sizer (SMPS, TSI, Inc., classifier model 3080, CPC model 3772). Non-refractory particle mass and chemical composition were measured with a quadrupole Aerosol Mass Spectrometer (AMS, Aerodyne, Inc.). Gas-phase organic species were measured with a proton transfer reaction mass spectrometer (PTR-MS, Ionicon) operated in selected-ion mode with a time resolution of ~2.5 min. The PTR-MS was calibrated daily using a custom gas standard from Spectra Gases. Dedicated gas monitors were used to measure CO₂ (LI-820, Li-Cor Biosciences), SO₂, NOx, CO, and O₃ (API-Teledyne Models 100E, 200A, 300A and 400E); monitors were zeroed daily and calibrated at least weekly. A seven channel aethalometer (Magee Scientific, Model AE-31) measured black carbon (BC), and the aethalometer attenuation measurements were corrected for particle loading effects using the method of Kirchstetter and Novakov [27].

Hydroxyl radical (OH) levels in the chamber were inferred from the decay of VOCs (e.g., toluene, xylenes, TMB, propene) measured with the PTR-MS [28]. In 21 of the 29 experiments 0.06 ppm of deuterated butanol was injected into the chamber; this compound provided very clear (little interference from other reactions) OH exposure data and did not form SOA. Typical experiment average OH levels were 5×10^6 molecules cm⁻³, which is within the range of summer daytime atmospheric concentrations [29]. OH levels were generally higher during the initial stages of the photo-oxidation phase of the experiment and then fell as the HONO was photolyzed.

2.3.3 Data Analysis

Pollutant data are reported on a fuel basis (mg pollutant /kg fuel):

$$EF = \frac{[P]}{[CO_2]} \cdot \frac{MW_{CO2}}{MW_C} \cdot C_f \tag{1}$$

where *[P]* is the background corrected pollutant concentration in $\mu g/m^3$, *[CO2]* is the background corrected concentration of CO₂ in the chamber in $\mu g/m^3$, MW_{CO2} is the molecular weight of CO₂ (44.1 g/mol), MW_C is the molecular weight of carbon (12 g/mol) and C_f is the measured carbon intensity of the gasoline (0.85 kg-C/kg-fuel). The carbon contribution from CO and HC was negligible in comparison to CO₂ in every experiment, so it was not necessary to include these species in calculating the emission factors.

The fragmentation table from Allan et al. [30] was used to interpret AMS data. The contribution of gas-phase CO₂ to the AMS m/z 44 signal was corrected using the measured CO₂ concentrations as a function of time. Maximum CO₂ levels in the chamber after exhaust injection ranged from 515 to 890 ppmv. There was no evidence of organic particle signal at m/z 28 (CO⁺). Organic and inorganic nitrates fragment into NO⁺ and NO₂⁺ in the AMS, but organic nitrates generally have a considerably higher ratio of NO⁺ to NO₂⁺, making it possible to apportion nitrate signal between the two classes. Using the approach of Farmer et al. [31], only a minor fraction (typically <5%) of the nitrate mass (which was usually quite small) was attributable to organics.

All CVS and chamber data are blank-corrected by subtracting the mass collected on a filter sample of the CVS air with no vehicle emissions, and the uncertainty of these measurements was estimated to be the greater of (a) 25% of the average value or (b) 1 mg/mile.

2.3.4 Quantifying SOA Production

To quantify SOA production in the smog chamber we corrected the measured concentrations of suspended particles for (a) the loss of organic particles and vapors to the chamber walls, (b) the increase in the particle loss rate for experiments in which nucleation occurs, and (c) the lower particle detection efficiency by the aerosol mass spectrometer (AMS) for particles smaller than about 60 nm. Wall loss corrections (1) are important in every experiment, whereas corrections for (b) and (c) are significant only for experiments when photooxidation induced nucleation, causing chamber concentrations to be dominated by smaller particles. Correction (a) is described below; corrections (b) and (c) are described in the SI.

Organic particles and vapors are lost to the chamber walls as a function of time, and total OA is the sum of the measured (via the AMS) suspended mass plus the mass of organics on the chamber walls

$$OA_{total,t} = OA_{sus,t} + OA_{wall,t} \tag{1}$$

Organics may be lost to the chamber walls as particles or vapors. Loss of organic particles is treated as a first-order process [31] with a rate constant determined from the decay of BC measured by the aethalometer

$$C(t) = C_0 e^{kt}$$

where *C* is the BC concentration at time *t*, C_o is the initial BC concentration and *k* is the wall loss rate constant. The wall loss rate constant depends on the size and composition of the particles, turbulence in the chamber, the size and shape of the chamber, and particle charge [32]. Therefore, it was determined for each experiment by fitting each time series of BC data. The average particle wall loss rate for all the experiments was -0.400±0.095 hr⁻¹ (i.e., after approximately 2.5 hr the BC concentration decreased to 37% of its initial value). For experiments without enough BC to calculate a rate constant the decay of (1) sulfate from the seed particles, (2) nitrate, (3) organics after photo-oxidation or (4) total PM after photo-oxidation was used.

Using BC (or any of the other species) as a tracer for wall loss assumes that it is internally mixed with the OA. This assumption was valid for most experiments because the size resolved data (SMPS and AMS) only showed growth of the primary mode aerosol. However, the majority of particle mass in the two regeneration experiments was formed from nucleation. Therefore, in these experiments it was necessary to adjust the wall loss rate to account for the more rapid loss of smaller nucleation mode particles. This correction is discussed in the SI.

It is possible that SOA production during our experiments could cause interference with the BC measured with the aethalometer at 880 nm, thereby complicating our reliance on this instrument for determining wall loss rates. To investigate this possibility we performed similar experiments in 2011, using a single particle soot photometer (SP2, DMT, Inc.) operating in parallel with the aethalometer. The results from the two instruments showed excellent agreement: average difference between the wall loss rates calculated from the aethalometer and the SP2 was 4% (n=8). The two instruments operate according to entirely different principles: the aethalometer measures light adsorption caused by BC collected on a filter, whereas the SP2 measures the laser-induced incandescence of individual BC particles. The close agreement between them strongly indicates the robustness of the BC values we used to calculate wall loss rates.

The loss of condensable organic vapors to wall-bound particles is constrained by considering two limiting cases: the first (Method #1) assumes that no organic vapors condense to

wall-bound particles, and the second (Method #2) assumes that organic vapors remain in equilibrium with both wall-bound and suspended particles. The loss of organic vapors directly to the chamber walls (in distinction to their loss to wall-bound particles) is highly uncertain, and in keeping with virtually every other chamber study in the literature, we do not account for it here. If it were included, it would *increase* our estimate of SOA production.

Method #1 provides a lower bound estimate of the SOA mass production; it is equivalent to the " $\omega = 0$ " correction utilized in previous studies [14, 17]. Method #1 assumes that mass transfer resistance to the walls is much greater than to the suspended particles. This is a reasonable assumption since condensable vapors are in continuous, intimate contact with suspended particles, whereas their interaction with wall-bound particles is likely to be far less frequent. A consequence of this wall loss assumption is that suspended and wall-bound particles may have different compositions.

Assuming no loss of vapors to the walls in Method #1, the rate at which OA mass is lost to the chamber walls is

$$\frac{d}{dt}(OA_{wall}) = OA_{sus}(-k) \tag{2}$$

where OA_{sus} is the AMS-measured (i.e., suspended) OA mass at time *t* and *k* is the negative wall loss rate constant of black carbon [14]. The total OA in the chamber is calculated by numerically integrating equation (2) and adding the calculated OA lost to the wall to the measured OA concentration (equation (1)).

Method #2 assumes that particles lost to the walls during an experiment remain in equilibrium with the vapor phase. This case corresponds to the " $\omega = 1$ " correction [14]. The

total OA mass at time t is equal to the suspended particle mass scaled by the ratio of the initial black carbon concentration to the black carbon concentration at time t

$$OA_{total,t} = OA_{sus,t} \cdot \frac{C_0}{C_t} \tag{3}$$

where C_o is the initial black carbon concentration and C_t is the measured black carbon concentration at time *t*. As only *suspended* OA is referenced in equation (3) the PM on the wall and in suspension has the same composition.

In experiments with low BC concentrations, the total OA estimates from Method #2 can be noisy due to their inverse dependence on BC in equation (3). For such experiments, we implemented Method #2 using the previously described exponential fit to the BC data rather than the actual BC data themselves,

$$OA_{total,t} = \frac{OA_{sus,t}}{e^{kt}} \tag{4}$$

where *k* is the negative wall loss rate constant of black carbon.

Experiments of Weitkamp et al. [14] indicate that the rate of vapor uptake to particles on the walls is the same as the rate for suspended particles (Method #2), suggesting that the mass transfer resistance of organic vapors to wall-bound particles is comparable with that to suspended particles. Equation (3) and Equation (4) indicate that in Method #2 the loss of organic vapors to particles on the walls scales with the mass fraction of particles on the walls to particles in suspension. Initially (before any particle loss) there is no loss of vapors to wall but it increases as an experiment progresses. Therefore, estimates based on Method #1 and #2 diverge as more particles are lost to the wall, and the uncertainty in the observed SOA production increases as an experiment progress [33]. Given this increasing uncertainty, we imposed a 5:1 upper bound on the ratio of OA on the wall to suspended OA. This condition was binding in less than half the experiments, and when it was binding, it was typically only later in the experiment after 1.5-2.5 hours of photo-oxidation. The average and range of OA from Methods #1 and #2 is reported in the results.

Chamber blank experiments performed after filling the chamber with CVS dilution air, HONO, and ammonium sulfate seed particles produced 1-3 μ g/m³ of SOA over a 3 hour photooxidation period. This SOA is likely formed from the residual vapors that desorb from the CVS, transfer line and chamber wall. Therefore, for every chamber experiment we assume an SOA blank of 0 μ g/m³ at t=0 that increases linearly to 2 μ g/m³ of SOA at t=3 h and subtract this artifact from the reported SOA production.

2.4 Results and Discussion2.4.1 Primary Emissions from the CVS: Comparison of ChamberVehicles and the Larger Fleet

One of the overall goals of this campaign was to quantitatively characterize the SOA production from light duty vehicles using a smog chamber. Sixty-three of the 64 unique vehicles in the larger fleet were tested in the base configuration, i.e., cold start UC; the remaining vehicle was excluded from these results because it was tested on a different driving cycle. The chamber experiments were performed on a subset of vehicles from the larger fleet. An important question is, then, How representative was the chosen subset? To answer this Figure 2.3 presents comparative data for the chamber experiments and the entire fleet. The figure summarizes total primary PM, its organic carbon (OC) and elemental carbon (EC) constituents and the non-methane organic gases (NMOGs) for the 15 gasoline vehicles tested in the chamber. The

individual data points for the chamber vehicles— pre-LEV experiments (3 unique vehicles, black circles), LEV-1 gasoline experiments (6 unique vehicles, blue circles) and LEV-2 gasoline experiments (6 unique vehicles, red circles)—are superimposed on a box-whisker plot of the data from all 63 gasoline vehicles tested in this campaign. Data in the box-whisker plot are grouped by vehicle emission standard: pre-LEV (MY1987-1993), LEV-1 (MY1994-2003) and LEV-2 (MY2004-2012). CVS POA—discussed in the report section below entitled "Primary and Secondary Emissions from Chamber Vehicles"—was estimated by assuming a POA to OC ratio of 1.2 [32].

PM emissions are dominated by carbonaceous material. Although there is significant vehicle-to-vehicle variability in primary emissions, Figure 2.3 indicates that for the overall fleet, there is a clear reduction in emissions for newer, lower mileage vehicles that meet more stringent emission standards. However, Figure 2.3 also shows that certain vehicles chosen for chamber tests were not representative of the trends of the larger fleet. For example, two of the LEV-1 chamber vehicles, the LEV1-1.5 and LEV1-6.1 vehicles, were responsible for the lowest and highest outliers for total primary PM among all the LEV-1 vehicles. The emissions control system of the LEV1-6 vehicle was known to be malfunctioning, leading to more variability in its performance and to higher emissions of EC and OC; for this reason it is referred to as a "high-emitter." While the LEV-1 chamber results included some values closer to the median, more of the LEV-1 measurements were outliers than the pre-LEV or LEV-2. For the larger fleet a factor of 3 reduction in total primary PM from pre-LEV to LEV-2 vehicles was driven primarily by an order of magnitude reduction in OC, while EC reductions were modest. Overall, the chamber vehicles reasonably mirror the trends of the larger fleet: NMOG, PM and OC were lower for

newer vehicles, but EC did not change systematically with emission standard. Further discussion of the primary emissions for the larger fleet can be found in [21].



Figure 2.3. Primary emissions from light duty gasoline vehicles tested in the smog chamber shown as individual data points overlaying boxplots of the data from every baseline vehicle experiment (including both primary only and primary+chamber experiments). Multiple experiments with the same vehicle were averaged before plotting, leaving data from 63 unique vehicles (15 pre-LEV, 23 LEV-1 and 25 LEV-2) for the boxplots. Baseline experiments all utilized the cold start unified driving cycle (UC). The 15 chamber experiments include: 3 unique pre-LEV vehicles (black circles), 6 unique LEV-1 vehicles (blue circles) and 6 unique LEV-2 vehicles (red circles). (a) Total primary PM from gravimetric analysis, (b) OC and (c) EC components of primary PM from thermal-optical analysis of quartz filters and (d) non-methane organic gases. The central marks on the boxplots are medians, the edges of the boxes are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers (>1.5 x interquartile range) are plotted individually with the "+" symbol.

2.4.2 Time Series of a Typical Chamber Experiment

Figure 2.4 illustrates the measured temporal evolution of both particle- and gas-phase species during a typical smog chamber experiment. There are three distinct periods in the experiment. First, vehicle emissions are added to the chamber throughout the entire UC test (38

minutes), increasing the pollutant concentrations inside the chamber. The engine was shut off at time = -1.0 hours, and HONO was added to the chamber at approximately time = -0.5 hours, modestly increasing NO₂ concentrations. Propene was also added (between 0.1 and 3.0 ppm, depending on initial VOC concentration in chamber) at this time. The loss of POA to the walls of the chamber is evident from the decay of the organic signal measured with the AMS (blue points in Figure 2.4c) occurring between the time when the engine is turned off and before the lights are turned on (time = 0 hours).

After the UV lights were turned on, the measured organic aerosol concentrations increased for about an hour and half, indicating substantial SOA formation. In contrast, the uncorrected (for wall losses) concentration of non-reactive black carbon decreased. (Due to interference during the HONO addition, BC measurements before lights were turned on are not shown.) After 3 hours the wall loss corrected organic concentrations increased by roughly a factor of 6 as ~2 μ g/m³ of POA increased to ~12 μ g/m³ (gray shaded region in Figure 2.4c). During the 3 hours of UV irradiation much of the NO and primary hydrocarbons are oxidized to NO₂ and more oxygenated VOCs, respectively (Figure 2.4a-b).

The wall-loss corrected OA concentrations roll over to a constant value late during the photo-oxidation experiment, potentially suggesting that SOA formation is complete. However, Figure 2.4b indicates that xylene and TMB concentrations stopped decaying after ~1.5-2 h, which suggests that the decrease in SOA production is probably due to decreased oxidant concentrations, rather than exhaustion of the gaseous SOA precursors.



Figure 2.4. Gas and particle evolution during a typical smog chamber experiment (LEV1-6.2 experiment). Between -1.5 hr < time < -1.0 hr, the chamber was filled with diluted emissions from the vehicle; for -1.0 hr < time < 0 hr, the primary PM was characterized; for time > 0 hr, the UV lights were on and photo-oxidation generated SOA. Concentrations of NOx, O_3 and CO_2 are shown in (a). Shown in (b) are the concentrations of two oxygenated VOCs which increase for time > 0 hr due to oxidation with the OH radical and/or O_3 in the smog chamber and two non-oxygenated VOCs which are consumed by the OH radicals. Shown in (c) are uncorrected and corrected (for wall losses) organic PM and black carbon concentrations; the large increase in organic PM mass is due to SOA production. The organic concentrations were corrected using two different methods (thus the gray shaded area) which provide an estimate of the uncertainty of the SOA production.

2.4.3 Primary and Secondary Emissions from Chamber Vehicles

Figure 2.5 summarizes the particle-phase data from 22 smog chamber experiments with 14 different vehicles. The experiments are grouped by emission standard (pre-LEV, LEV-1, LEV-2). Figure 2.5a plots the BC and POA emissions measured in the CVS and the wall loss corrected SOA (average of the two methods of wall loss correction) measured in the chamber at the end of the experiment (after three hours of photo-oxidation). Figure 2.5 b presents the ratios of the wall loss corrected SOA to the CVS POA and the SOA to total primary PM. The comparison with primary PM is important because this is the quantity (not POA) that is currently regulated in vehicle emissions standards.



Figure 2.5. (a) Median amount of BC, POA (measured in the CVS), primary PM (measured in the CVS) and SOA (average from the two wall loss correction methods) for 22 chamber experiments, classified by emission standard (pre-LEV, LEV-1 and LEV-2). (b) Median ratios of SOA to POA (measured in the CVS) and SOA to primary PM (measured in the CVS), classified by emission standard (pre-LEV, LEV-1 and LEV-2). All SOA values are taken after 3 hours of photo-oxidation. The dashed horizontal line in (b) represents 1:1. Error bars represent uncertainty propagated through all measured variables (calculation described in Data Analysis section).

Gas-particle partitioning is a function of both temperature and particle concentration, and

it can significantly alter the measured concentrations of primary and/or secondary aerosol.

Though particle concentrations in the CVS varied they were almost always much higher than the

ambient, biasing our measurements toward higher particle concentrations. Further discussion of partitioning can be found in [33].

Figure 2.5a indicates that there has been a large reduction in POA and primary PM for newer vehicles (i.e., LEV-1 and LEV-2), which is consistent with the OC and NMOG data shown in Figure 2.3b and d. The POA from LEV-2 experiments is comparable to or slightly less than LEV-1 vehicles. Although in Figure 2.5a the BC levels are lowest for LEV-1 vehicles, the EC data shown in Figure 2.3c, indicate that this is likely due to the smaller sample size of vehicles tested in the chamber (where the BC was measured). There is no significant difference in BC between pre-LEV and LEV-2 vehicles. The error bars for the LEV-1 vehicle in Figure 2.5a are large because they include data from the LEV1-6 vehicle which had a malfunctioning emission control system; it was considered a "high-emitter."

While median SOA estimates in Figure 2.5a indicate that LEV-1 and LEV-2 vehicles produced less SOA, the uncertainty is fairly large, and it is likely that the estimates do not differ significantly. (When the average rather than the median SOA values are plotted, the three SOA values differ less.) Assuming the difference is not significant (and there is certainly not a significant difference between LEV-1 and LEV-2) suggests that, while tighter emission standards are clearly reducing POA (also evident for the larger fleet in Figure 2.3), they may not be effectively reducing SOA from gasoline vehicles.

Figure 2.5b shows that the mass of SOA (produced after 3 hours of photo-oxidation at atmospherically relevant conditions) is greater than primary PM in the LEV-1 and LEV-2 experiments; median ratios are 6 and 3, respectively. Figure 2.5b illustrates a qualitatively similar pattern for the magnitude of SOA to the POA measured in the CVS. SOA/primary PM ratios for several of the LEV-2 experiments were smaller than SOA/POA ratios for the same

experiments because the primary PM emissions from these vehicles are dominated by BC rather than POA.

Overall, Figure 2.5 suggests two reasonably distinct behaviors for the three vehicle categories. Pre-LEV vehicles clearly emit much higher primary PM than the other two categories, but SOA produced after photo-oxidizing pre-LEV emissions, appears to differ much less. While SOA production from pre-LEV vehicles is sizeable, almost doubling the mass of the net PM, SOA is much more important when considering the LEV-1 and LEV-2 vehicles.

Nine sets of duplicate chamber experiments were run (data not shown), and in 6 of these the measured SOA, POA and BC agreed, suggesting good repeatability for the experiments in this campaign. SOA production with the LEV1-6 vehicle varied considerably in two duplicate experiments (LEV1-6.1 and LEV1-6.2), but the EC and POA were very similar. The variability in the SOA for the LEV1-6 duplicates may indicate that the gaseous precursor emissions for this vehicle (which was known to have emissions control problems) were more variable than its primary particle emissions. Indeed, this turns out to be the case as we discuss in the following section which investigates the variation in SOA production among the chamber experiments.

2.4.4 SOA Yield

In this section we investigate the variability in SOA formation observed for the different chamber experiments. SOA formation depends on oxidant exposure and gaseous precursor concentrations. We consider each of these factors in turn.

SOA as a function of OH exposure (i.e., [OH] multiplied by the exposure time) is plotted in Figure 2.6 for selected (to reduce clutter) vehicles. Summertime OH concentrations typically range from $5-10x10^6$ molecules cm⁻³ [29]; therefore, these experiments correspond to approximately 1.5-3 hours of atmospheric aging under typical summertime conditions. SOA production is roughly linear with OH exposure for most experiments. The inset in Figure 2.6 shows that for a representative experiment (the LEV1-6.2) when OA production is plotted as a function of OH exposure (red, upper x-axis) rather than as a function of time (black, lower x-axis) it does not rollover; the red curve goes up linearly until the OH exposure plateaus (causing the data points to "bunch up" rather than rollover). This provides further evidence that the reduced rate of SOA production for t > 1 hr observed in Figure 2.4b is due to decreased oxidant concentrations, rather than exhaustion of the gaseous SOA precursors.



Figure 2.6. SOA (average of the two wall loss correction methods) as a function of OH exposure for 8 chamber experiments. LEV-I vehicles are represented by open circles; LEV-2 vehicles are represented by filled triangles.

Inset shows that the rollover observed when organic aerosol production is plotted as a function of time (black, lower x-axis), is eliminated when OA is plotted as a function of OH exposure (red, upper x-axis); the LEV1-6.2 experiment shown in the inset is typical. A four period moving average is used to smooth both data sets plotted in the inset. Data for pre-LEV vehicles and other experiments are not shown to reduce clutter in the figure. SOA vs. OH exposure is not linear for the LEV1-1 experiment due to the low primary particle emissions: without adequate surface area from the primary particles, vapor loss to the chamber walls was especially large in this experiment.

Figure 2.6 shows that for the same OH exposure the LEV1-6.2 experiment generated the greatest amount of SOA among all the experiments shown here. This result suggests that variations in SOA production cannot be attributed to OH exposure. Therefore, we investigated whether experiment-to-experiment variations in SOA procursor concentrations were driving SOA production rather than differences in OH exposure.

Traditional SOA precursors include monoterpenes, dominant globally due to very high biogenic emissions; single-ring aromatics such as toluene, benzene and xylenes, which are found in combustion emissions from many fuels; and lower volatility VOCs. To investigate the effect of precursor concentrations on SOA production, SOA was divided by the sum of the changes in each of the traditional anthropogenic SOA precursors (from the speciated NMOG data) and plotted against OH exposure in Figure 2.7. The precursors in this yield include single-ring aromatics (C_6 to C_{12}) and mid-weight VOCs (C_9 to C_{12}). The change in the concentration of each of the speciated precursors was calculated from its initial concentration (measured in the CVS), the OH exposure and the reaction rate for the species with OH. There are several important observations from this figure. First, the highest SOA producing experiment—the LEV1-6.2 experiment (Figure 2.6a)—has one of the lowest SOA yields. Furthermore, the newer LEV-2 vehicles (represented by the filled triangular symbols) tested in this work have higher SOA yields than older LEV-1 vehicles. Second, by assuming that only traditional precursors photo-

oxidize to form SOA, the calculated yields are unrealistically high. Yields greater than unity for some of these experiments clearly indicate that additional precursors are required for mass closure.



Figure 2.7. SOA yields from known SOA precursors (single-ring aromatics (C_6 to C_{12}) and mid-weight VOCs (C_9 to C_{12})) for 7 chamber experiments. Other experiments could not be plotted because speciated NMOG data were not available. LEV-I vehicles are represented by open circles; LEV-2 vehicles are represented by filled triangles. Data for pre-LEV vehicles and other experiments are not shown to reduce clutter in the figure.

Other studies have also demonstrated that traditional SOA precursors are not capable of explaining the amount of SOA formed from the combustion products of various fuels, including wood, diesel and jet fuel [14, 17, 34]. Even after increasing the SOA yields of traditional precursors to reflect the most recent literature values, Robinson et al. found that these precursors were only able to account for one quarter or less of the measured SOA from wood smoke and diesel fuel [12]. These chamber studies as well as studies which have found higher ambient

SOA concentrations than can be explained by traditional precursors, provide strong evidence that additional, species contribute to SOA production. For example, Robinson et al. argued that SVOCs and IVOCs are responsible for substantial SOA production [35]. Therefore, in addition to the yield from traditional precursors shown in Figure 2.7 ("Case 1"), we consider three other yield cases:

- 1. Case 1 (traditional)—known precursors, including single-ring aromatics (C_6 to C_{12}) and mid-weight VOCs (C_9 to C_{12}). Reaction rates were taken from published measurements or models.
- 2. Case 2—precursors in case 1 + SVOCs and IVOCs. S/IVOCs were lumped together and assumed to react at $3x10^{-11}$ cm³ molecule⁻¹ sec⁻¹.
- 3. Case 3—precursors in case 2 + the unspeciated NMOGs, defined by subtracting all the speciated NMOGs and the S/IVOCs from the NMOG measurement. The unspeciated NMOGs were lumped together and assumed to react at 1x10⁻¹¹ cm³ molecule⁻¹ sec⁻¹.
- 4. Case 4—precursors in case 3 + all remaining speciated NMOGs, including all nonaromatic C₂ to C₈ compounds. Reaction rates were taken from published measurements or models.

Yields decrease in the direction of increasing yield case number, as would be anticipated since more species are assumed to react in each case. Plots similar to those in Figure 2.7 were created for Cases 2-4 (not shown here), and the best yield estimates for experiments with complete NMOG data are plotted in Figure 2.8 for each of the four cases. The error bars show the span in yields calculated by two extreme sets of assumptions. The lower bounds are based on scenarios resulting in low SOA estimates and high masses of reacted precursors: they do not incorporate the AMS collection efficiency or nucleation wall loss corrections; assume the chamber blank=3 μ g/m³ (at t = 3 hr); use wall loss correction Method #1 and increase the S/IVOC mass by a factor of 3. The upper bounds are based on scenarios resulting in high SOA estimates and low masses of reacted precursors: they incorporate the AMS collection efficiency

and nucleation wall loss corrections; assume the chamber blank= $0 \mu g/m^3$; use wall loss correction Method #2 (high SOA estimate) and reduce the available S/IVOC mass by a factor of 3.

Figure 2.8 indicates that incorporating the S/IVOCs in the yield estimate (Case 2) reduces the yields only slightly from 4-18% to 3-16% for LEV-1 and from 57-245% to 51-161% for LEV-2. However, including the unspeciated NMOGs has a much larger impact: the Case 3 (best estimates) yields range from 2-8% for LEV-1 and 19-83% for LEV-2. The yields are reduced further in Case 4 but not as dramatically as the difference between Case 2 and Case 3. While the best estimate for the LEV2-4.2 experiment in Figure 2.8 is perhaps still somewhat high, overall Case 3 provides a plausible explanation for the observed SOA production.

Over the time scale of these experiments, the mix of organic vapors emitted by newer vehicles is more efficient (higher yielding) in producing SOA than the emissions from older vehicles. In addition to the important role of unspeciated NMOGs already discussed, this result is sensitive to OH exposure estimates. For example, the best Case 3 yield estimate for the LEV2-1 experiments (the yields from the duplicate experiments are very close) is 65%. If the OH exposure used in calculating the yield is adjusted to the average $\pm 1\sigma$, the Case 3 yields for this vehicle become 50% and 115%, respectively.



Figure 2.8. Four different yield estimates for 7 experiments with speciated NMOG data. Bars indicate best estimate. Upper uncertainty range incorporates the AMS collection efficiency and nucleation corrections and also assumes the chamber blank=0 μ g/m³, wall loss correction Method #2 (high SOA estimate) and reduces the available S/IVOC mass by a factor of 3. Lower range of uncertainty does not incorporates the AMS collection efficiency or nucleation corrections; it assumes the chamber blank=3 μ g/m³ (at t = 3 hr) wall loss correction Method #1 (low SOA estimate) and increases the available S/IVOC mass by a factor of 3.

Data from additional light duty gasoline experiments were very recently provided by

CARB, but there was not enough time to revise Figure 2.8 to reflect these data before submitting the thesis. Instead, the yield data from all the chamber experiments (including those shown in Figure 2.8) were compiled and the medians and standard deviations for pre-LEV, LEV-1 and LEV-2 vehicles are plotted in Figure 2.9. This figure is based on the Case 3 SOA yields described above. It includes the experiments shown in Figure 2.8 as well as the newest data. Figure 2.9 shows the clear increase in SOA yields for newer LEV-1 and LEV-2 vehicles compared to the pre-LEV vehicles.



Figure 2.9. Median SOA yields for pre-LEV, LEV-1 and LEV-2 light duty gasoline vehicles. The median values are based on yield case 3, which is assumed to be the best estimate. Error bars represent the standard deviations of the medians. "N" represents number of experiments used for each vehicle class, and the number of different vehicles is in parentheses.

To investigate the variability in SOA yields, we consider the SOA production in the context of the VOC data. Figure 2.10 indicates that approximately 62-84% of the NMOGs from the LEV-1 and LEV-2 vehicles were speciated. (Additional experiments, including those with pre-LEV vehicles were performed but the data has not yet been provided by CARB.) This level of mass closure is similar to results of Schauer et al. [13, 36].

The data in Figure 2.10 suggest a trend toward decreasing emissions of SOA precursors and unspeciated NMOGs with newer vehicles (in agreement with Figure 2.3), but the relative amount of SOA precursors has remained approximately constant at about 20% of the NMOG mass. The combination of lower absolute levels of SOA precursors and unspeciated OCs for LEV-2 vehicles reinforces the conclusion drawn from Figure 2.9, namely, that LEV-2 yields are greater than LEV-1. Figure 2.10 shows that the LEV1-1 vehicle emitted more SOA precursors and more unspeciated NMOGs than the LEV-2 experiments, but it generated approximately the same amount of SOA as them. The lower than expected SOA production for the LEV1-1

experiment may be due in part to higher vapor loss to the walls (as previously discussed). It is also plausible that the composition of the unspeciated fractions differ significantly and that these differences are partially responsible for the variation in SOA yields, especially since the speciated OCs do not explain the differences in SOA production from different vehicles.



Figure 2.10. Non-methane organic gas (NMOG) emissions for selected chamber experiments. Note that data for many of the experiments (including pre-LEV experiments) have not yet been provided by CARB. The emissions have been lumped into three broad categories: (1) SOA precursor OCs, including single-ring aromatics (C_6 to C_{12}), mid-weight VOCs (C_9 to C_{12}), IVOCs (C_{13} to C_{18}) and SVOCs (C_{19} to C_{38}); (2) unspeciated OCs and (3) non-SOA precursor OCs, including methane, non-aromatic carbonyls (C_1 to C_8) and light VOCs (C_2 to C_8). The emission factors for the two shaded experiments have been divided by 10x for ease of display. NMOGs were measured in the constant volume sampling system upstream of the chamber.

2.4.5 SOA Composition

The AMS provides information on the composition of the organic aerosol. Figure 2.11 plots OA composition measured by the AMS after 0 hr (fresh OA) and 3 hr (aged OA) of UV exposure. It illustrates the evolution of emissions from the tailpipe to the ambient atmosphere via oxidative processing. The average spectra of both fresh and aged OA in Figure 2.11a are dominated by the ion series associated with hydrocarbons: straight and branched alkanes at
$C_nH^+_{2n+1}$ (*m/z* 29, 43, 57, ...) and cycloalkanes at $C_nH^+_{2n-1}$ (*m/z* 27, 41, 55, 69, ...) and $C_nH^+_{2n-3}$ (*m/z* 67, 81, 95, ...) [37, 38]. Consistent with previous studies of SOA production from dilute diesel combustion emissions [14], Figure 2.11a shows that the aged OA is dominated by smaller fragments, indicative of a trend toward greater fragmentation of the aged aerosol. In a typical experiment such as the LEV1-6.2 experiment shown in Figure 2.11b the *m/z* fragments characteristic of more highly oxidized species such as *m/z* 31 (CH₃O⁺) and *m/z* 44 (CO₂⁺) show a clear increase with aging, while the fragments associated with fresh emissions such as *m/z* 57 (C₄H₉⁺) and *m/z* 71 (C₅H₁₁⁺) decrease. The *m/z* 43 (mainly C₃H₇⁺ in the primary emissions and C₂H₃O⁺ in the SOA) fragment, associated with both fresh and aged emissions, decreases as shown in Figure 2.11b. Previous chamber studies have shown that *m/z* 43 remains constant during oxidation of diesel exhaust [14], while at least one single-chemical-component study has shown a decrease in *m/z* 43 with aging [39].

It is important to determine whether SOA produced in these experiments is similar in composition to ambient OA; therefore, we compare the values of f44—the fraction of the organic signal attributed to m/z 44—and f43 for the chamber OA to the values measured in ambient AMS studies. The dotted triangle in Figure 2.11c is taken from the work of Ng et al. [40] who use it to define the region in which ambient OA falls based on their analysis of 43 different datasets sampled from both rural and urban settings. F44 is expected to be greater in rural sites than in urban sites due to oxidation/aging during transport from pollution sources [8, 41]. The data from our work is generally consistent with this trend from the lower right (POA) toward the upper left (aged OA) of the triangle. This result indicates that OA in the smog chamber oxidizes, rapidly transforming into lower volatility, highly oxygenated OA typical of the ambient atmosphere.



Figure 2.11. (a) Average aerosol mass spectrum for vehicles tested in the smog chamber showing the fraction of the total organics in the chamber samples for each mass to charge ratio. Two time points are shown: just before lights on (time = 0 hr, blue bar) and after 3 hr of oxidation in the chamber (red square). POA average is based on data from 7 experiments in which POA > 1 μ g m⁻³. Aged OA average based on data from all 12 experiments. (b) Fraction of the total organic mass for selected *m*/*z* ratios for the LEV1-6.2 experiment; note that the f31 signal is multiplied by a factor of 10. (c) Fraction of organic mass due to *m*/*z* 44 vs. *m*/*z* 43. Triangular region defines the expected domain for ambient OA [40].

2.5 Conclusions

In summary, three hours of photo-oxidation of combustion emissions from gasolinefueled light duty vehicles produces large amounts of secondary organic aerosol on an absolute mass basis and in comparison to primary emissions. Although progressively more stringent regulations have reduced the primary pollutants emitted by motor vehicles, including major reductions in gas-phase hydrocarbons, SOA from both older (pre-LEV and LEV-1) and newer (LEV-2) gasoline vehicles remains comparable to or several times larger than total primary PM. In fact, the clear downward trend in primary organic PM only serves to highlight the importance of SOA: the newest vehicles in this test fleet had SOA/POA ratios between 15 and 20, compared to values closer to unity for the older gasoline vehicles.

Measured emissions from vehicles on the road are often considerably higher than the value for which they were designed – 1.5-2x higher on average [42]. Thus, an important aspect of the present work is its focus on vehicles from an in-use fleet, tested over a realistic driving cycle in a laboratory authorized to certify compliance with CA emissions standards. SOA from newer light duty vehicles is approximately 3-6 times greater than the primary PM that is currently being regulated. Furthermore, there is no evidence that SOA production was complete in these experiments after 3 hours (i.e. SOA was still being produced when we ended the experiments); therefore, the emissions are expected to undergo substantially more oxidation, producing even more SOA than we observed in these experiments and increasing the SOA/primary PM ratios. Other studies have shown that SOA production downwind of urban areas may persist for 48 hours [8, 43].

We calculate reasonable yields when unspeciated NMOGs were included as SOA precursors, and our analysis suggests that gas-phase emissions from LEV-2 vehicles are more efficient than pre-LEV and LEV-1 vehicles in producing SOA. The exact species responsible for these differences remain unknown. Differences in S/IVOC mass do not appear to explain the variations in SOA. SOA produced from the photo-oxidation of the emissions from these light duty vehicles is similar to the OA found in the ambient atmosphere and more oxidized than the POA.

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2.7 Supplementary Information

	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁₊
paraffins	0.69	9.12	11.45	11.62	12.8	3.05	1.27	2.29
aromatics			0.66	6.12	10.17	8.32	2.14	0.9
cyclic olefins		0.08	0.26	0.19	0.06	0.01		
olefins/naph- thalenes polynaph-	12.38							
thalenes	thalenes 0.22							
MTBE		6.2						
TOTAL (mass%)	100% = 84.97% C + 13.91% H + 1.12% O							

Table 2.4. Chemical analysis of gasoline used in all spark-ignition engine SORE experiments, listed as mass percentages per carbon number.

Table 2.5. Comparison of the unified cycle (UC) and FTP-75 cycle. The UC, used in this study, is a more aggressive cycle than the FTP.

driving cycle	duration (s)	distance (mi)	avg speed (mph)	max speed (mph)	max accel (mph/s)	stops/ mile	% idle	notes
UC	2035	9.8	24.6	67	6.15	1.52	16.4	600 s hot soak not included in avg speed or % idle values
FTP-75	1377	7.5	19.6	56.7	3.31	2.41	19	for comparison only; not used in this study

http://www.dieselnet.com/standards/cycles/hhddt.php http://www.arb.ca.gov/msei/onroad/briefs/Publication3.pdf

2.7.1 Wall Loss Rate Correction For Nucleation

Particle loss to chamber walls is a size-dependent process (smaller particles are lost faster); therefore, in experiments where a major fraction of the particle mass is created during a nucleation event, we must modify the wall loss rate to account for the more rapid loss of nucleation mode particles compared to BC (which is in the accumulation mode). In these cases a large fraction of the OA mass is not internally mixed with BC. Nucleation was an important factor in four of the chamber experiments. In the LEV1-1.5, LEV1-5.2, LEV2-1.2 and LEV2-2.1 experiments between 40% and 99% of the total OA mass in the chamber was in the nucleation mode within minutes of turning on the UV lights.

To illustrate the contribution of nucleation to the particle mass in the chamber, Figure 2.12 and Figure 2.13 present particle size distributions for experiments in which nucleation contributes negligibly and significantly to the total OA mass, respectively. Particle number and mass distributions for the LEV1-6.2 experiment at four different time points are shown in Figure 2.12. This was a high emitting vehicle; the primary PM concentration in the chamber after the vehicle driving cycle (from SMPS measurements, assuming unit density) was approximately 13 µg m⁻³. While nucleation does occur in this experiment—as evidenced by the large peak at about 20 nm in the number size distribution—only 3% of the particle mass is in the nucleation mode ten minutes after nucleation. Most of the secondary mass condenses onto accumulation mode particles. Nevertheless, the growth of the nucleation mode particles toward the primary mode still results in a shift in the mass distribution to smaller sizes than before nucleation, but it is slight and should not impact wall loss estimate from the BC data significantly.

In contrast, Figure 2.13 presents the size distributions for the LEV1-5 vehicle, a low emitting vehicle. The primary PM concentration in the chamber after the vehicle driving cycle (from SMPS measurements, assuming unit density) was approximately 2 μ g m⁻³. In Figure 2.13, the nucleation peak at 20 nm, formed -0.19 hr after the UV lights were turned on, completely dominates both the two primary particle number concentrations (the pre-nucleation number concentrations lie very close to the x-axis and can't be readily discerned in the figure because of the size of the nucleation peak) and the two primary particle mass concentrations. In this experiment, the nucleation mode contributed 63% of the total particle mass within 0.19 hr after lights on. The mass distribution for the LEV1-5 vehicle on the right side of Figure 2.13 show a major shift in the mass median diameter from about 190 nm for the primary PM emissions at t=0 h to about 32 nm at t=0.19 h occurs. Because of the dominant nucleation mode in this experiment, the wall loss rate of BC in the 190 nm primary mode is not a good model for the nucleated particles; if the BC wall loss rate were used to estimate the loss of the nucleated organics, we would substantially underpredict the actual SOA production.



Figure 2.12. Particle number (left) and mass (right) distributions for the LEV1-6.2 experiment (a) immediately after injection of emissions into the chamber ceased, (b) just before lights on, (c) at the beginning of a small nucleation event about 15 minutes after lights were turned on, and (d) 3 hours after lights were turned on.



Figure 2.13. Particle number (left) and mass (right) distributions for the LEV1-5 vehicle (a) immediately after injection of emissions into the chamber ceased, (b) just before lights on, (c) at the beginning of a very large nucleation event about 15 minutes after lights were turned on, and (d) 3 hours after lights were turned on.

In the four experiments where the nucleation mode contributes more than 25% of the suspended aerosol mass, we corrected the wall loss rate, k, for particle size. Our approach assumes that wall loss of nucleation mode particles is governed by Brownian diffusion. Crump and Seinfeld derived an expression for the size-dependent wall loss rate for particles in a spherical chamber of radius *R*

$$k_w(D_p) = \frac{6\sqrt{k_e D}}{\pi R} D_1\left(\frac{\pi v_s}{2\sqrt{k_e D}}\right) + \frac{v_s}{4R/3}$$
(1)

where *D* is the Brownian diffusivity for particles of diameter D_p , k_e (units of time⁻¹) is a function of the turbulent kinetic energy in the chamber, v_s is the gravitational settling velocity of the particle (negligible for nucleation mode particles) and $D_1(...)$ is the Debye function [44].

Equation (10) indicates that the wall loss rate scales with the square root of diffusivity, which in turn, is inversely proportional to particle diameter [29]. We therefore scale the wall

loss rate of the nucleation mode, k_{nuc} , using the wall loss rate of the primary mode, k, and the diameters of the nucleation mode, d_{nuc} , and the primary mode, d

$$k_{nuc} = k \cdot \sqrt{\frac{d}{d_{nuc}}} \tag{2}$$

Figure 2.14 illustrates the impact of correcting for the more rapid loss of nucleation mode particles on the organic aerosol estimates. There is $\approx 20\%$ increase in OA when the nucleation correction is employed with wall loss correction method #1 and about a $\approx 50\%$ increase for Method #2. The relative changes shown in Figure 2.14 are comparable for the other experiments with a significant nucleation mode.



Figure 2.14. Wall loss-corrected OA for the LEV2-2.1 vehicle with and without nucleation correction.

2.7.2 AMS Corrections: Comparison with SMPS Measurements

Theoretically, the sum of the PM mass from the non-refractory components (measured by the AMS) and BC (measured by the aethalometer) should be equal to the mass calculated from

the SMPS size distributions. These three sets of data provide two independent methods of calculating PM, but each method has limitations, complicating the comparison.

First, the SMPS measures particle mobility diameter, while the AMS measures mass. To convert SMPS measurements to mass one must assume a particle shape and density. We assume that particles are spherical with average density of 1 g/cm³. However, fractal-like particles will cause the SMPS to overestimate the spherical equivalent diameter and therefore overestimate particle mass. While commonly made, the unit density [45] and sphericity [46, 47] assumptions have both been shown to not always be valid for aerosol with high EC (e.g., diesel emissions). After SOA production begins the sphericity assumption improves as the organics coat the primary particles, making them more spherical [48].

Second, the mass measured by the AMS will be less than the true PM mass due to three artifacts whose product is referred to as the AMS collection efficiency:

$$C_e(d_{va}) = E_L(d_{va}) \times E_S(d_{va}) \times E_B(d_{va})$$
(3)

where d_{va} is the particle vacuum aerodynamic diameter. The transmission efficiency, E_L , of the AMS's aerodynamic lens is size-dependent with a detection window that falls off above 600 nm and below 120 nm [49]. E_S is the striking efficiency, which refers to the tendency of non-spherical particles to miss the AMS's vaporizer as they are conveyed from the time-of-flight chamber. E_B quantifies the fraction of particles that bounce off of the AMS's vaporizer before they are measured. Bounce is a function of particle phase (solid/liquid), particle acidity and ambient RH, among other factors. For an internally mixed aerosol (which is likely in these experiments once SOA forms), the same collection efficiency should be used for all chemical species [50]. Losses due to striking efficiency appear to be less than 20% for ambient particles [51].

For the four experiments with substantial nucleation, a large fraction of the particle mass was in the 10 nm $< d_{va} < 30$ nm range and, therefore, was not detected by the AMS. Thus, the calculated OA production in these experiments is likely to deviate from the true value due to (1) the increased wall loss rates experienced by nucleation mode particles, (2) the reduced AMS transmission efficiency of particles below the detection window and (3) other collection efficiency effects (i.e., E_S and E_B).

In addition to the four experiments with major nucleation events, there were other experiments with somewhat larger mass median particle sizes (80 nm $< d_{va} < 120$ nm); it was not necessary to correct the wall loss rates for nucleation in these experiments, but the collection efficiency effects were still important. In particular, some fraction of the particles in such experiments is not transmitted through the lens due to the AMS's size-detection limitations. Figure 3.9 presents an example of such an experiment. It shows that the sum of the nonrefractory components and BC for the LEV1-6.2 experiment are approximately a factor of two lower than the mass calculated from the SMPS size distributions (assuming spherical particles and density of 1 g cm⁻³). As previously discussed, while there is nucleation in this experiment (Figure 2.12), it has only a minor impact on the mass distribution—unlike the large nucleation effect found in experiments with behavior as described in Figure 2.13. Nevertheless, as this experiment demonstrates, the AMS detection window artifact can be important in experiments even when the nucleation event is small and does not have a major impact on the overall mass distribution (and thus the wall loss rate).

We assume that the discrepancy between the sum of the speciated masses and the SMPSderived mass shown in Figure 3.9 is primarily due to E_L . While it is possible that particle bounce and/or striking efficiency may be responsible for some of the discrepancy, we cannot readily deconvolve the three components of the collection efficiency, and, furthermore, even if we could, it is not obvious that correcting for them would require a different approach than the simplified approach we describe next.



Figure 2.15. Comparison of the sum of BC (measured by the aethalometer), organics, sulfate, nitrate and ammonium (measured by the AMS) against the total particle mass measured by the SMPS for the LEV1-6.2 experiment. Data are not wall loss corrected.

For those experiments with the AMS+BC vs. SMPS discrepancy, we assume that the difference in mass has the same chemical composition as the speciated components. We then calculate a scaling factor, $AMS_{s.f.}$, that increases the sizes of the four colored wedges in Figure 3.9 proportionally such that their sum closes the gap with the SMPS measurement (dashed line). The scaling factor is

$$AMS_{s.f.} = \frac{C_{SMPS} - C_{BC}}{C_{org} + C_{SO_4} + C_{NO_3} + C_{NH_4}}$$
(4)

where C_{SMPS} is the total particle concentration measured by the SMPS, C_{BC} is the black carbon concentration measured by the aethalometer, C_{org} , C_{SO_4} , C_{NO_3} , and C_{NH_4} are the concentrations of organics, sulfate, nitrate and ammonium measured by the AMS. The values for $AMS_{s,f}$ were calculated for each time step after nucleation, excluding the times when the aerosol passed through the thermodenuder, and then these values were averaged over the three hour UV exposure period. The $AMS_{s,f}$ was used to scale the AMS data for the LEV1-5.2, LEV1-6.1, LEV1-6.2, LEV2-1.6, LEV2-2.1 and LEV2-4.2 experiments. In these experiments the average $AMS_{s,f}$ ranged between 1.13 and 2.01, and the coefficient of variation within each experiment was between 7% and 18%. The $AMS_{s,f}$ was not used to scale the data from other experiments either because the larger median particle size didn't warrant it or because the $AMS_{s,f}$ was too uncertain (i.e., the COV was greater than 20%).

Chapter 3: Secondary Organic Aerosol Production from Diesel Vehicle Exhaust: Impact of Aftertreatment, Fuel Chemistry and Driving Cycle

3.1 Abstract

Environmental chamber ("smog chamber") experiments were conducted to investigate effects of photochemical aging on dilute emissions from two medium-duty diesel vehicles (MDDV) and three heavy-duty diesel vehicles (HDDV). The goal of the experiments is to investigate how emissions from the tailpipe transform in the ambient atmosphere. Vehicles were tested with a range of emission control aftertreatment (none, DOC, DOC+DPF, DOC+DPF+SCR), fuel types (biodiesel and low-, medium- or high-aromatic ULSD) and driving cycles (UC, UDDS, creep/idle). Vehicles with a diesel particulate filter and diesel oxidation catalyst (DOC+DPF) emitted very little BC and POA. Emissions from these vehicles were photo-oxidized in the smog chamber at atmospherically relevant hydroxyl radical concentrations (~5x10⁶ molecules cm⁻³) for three hours, but they produced much less (or no measurable) secondary organic aerosol (SOA) than vehicles without aftertreatment. However, significant SOA, BC, POA and sulfate were measured during forced DPF regeneration experiments. For both MDDV and HDDV without aftertreatment substantial SOA formed—with the emissions from some vehicles generating twice as much SOA as POA after three hours of oxidation at typical urban VOC:NOx ratios (3:1). For the HDDV without a DPF the SOA yield (estimated from the calculated oxidation of speciated non-methane organic precursor gases) was approximately 10%. While net PM (primary+secondary) and POA were comparable for 3xcreep+idle and higher speed urban operation, SOA production from 3xcreep+idle was 3-4 times larger than SOA production from the UDDS cycle. This increase in SOA production from 3xcreep+idle emissions was offset by lower BC emissions. Although the aromatic content of the emissions was positively correlated with the aromatic content of the three different ULSDs, the aromatic content of the fuels had no effect on primary PM or secondary PM production. Switching from ULSD to biodiesel reduced BC substantially while leaving POA and SOA unchanged. Although SOA production from diesel and biodiesel fueled vehicles without a DPF was significant on an absolute basis, the net PM from these vehicles was dominated by BC.

3.2 Introduction

Numerous ambient studies have shown that organic aerosol is a major component of atmospheric particulate matter (PM2.5) [1] and that secondary organic aerosol (SOA)—formed in the atmosphere from the oxidation of organic vapors—dominates the OA directly emitted from sources (primary organic aerosol or "POA") even in urban areas with substantial POA emissions [2-4]. However, the sources of OA remain inadequately characterized [1, 5], and chemical transport models parameterized by the existing data systematically underpredict SOA levels [6-8], especially in photochemical episodes [9], thereby significantly limiting their utility in defining effective PM control strategies. There is, therefore, a need to more clearly

characterize the POA and SOA (as well as other PM and gas-phase pollutants) arising from ubiquitous sources such as motor vehicles.

On-road vehicles comprise a large source of anthropogenic PM2.5 [10, 11]. According to the EPA, they emitted $>10^5$ tons of PM2.5 in the U.S. in 2008 [12], but this figure only represents the primary PM from cars and trucks. It does not include the SOA formed from the atmospheric oxidation of their gas-phase emissions, and historically, PM regulations for on-road vehicles have incrementally ratcheted down primary PM limits, while SOA precursors per se remain unregulated or indirectly regulated at best.

Both "bottom up" emission inventories [13, 14] and "top down" chemical mass balance receptor models [15, 16] have shown that PM emissions from diesel vehicles (primarily heavy duty diesel vehicles, HDDV) contribute more to ambient PM levels than gasoline vehicles. HDDV constitute only 4% of the number of on-road vehicles and 7% of VMT (in California's 2011 emission inventory), but studies have estimated that diesels contribute 25-60% of primary PM from motor vehicles [16, 17]. The breadth of this range indicates the considerable uncertainty in estimating the relative contribution of primary PM from diesel vehicles [18], but their role in SOA production is even less clear, owing to the paucity of data. SOA production from diesel emissions is a relatively new area of research, but there is evidence that it may be an important OA source [19-22]. For example, Chirico et al. found that emissions from a light duty diesel vehicle (LDDV) produced substantial SOA mass relative to black carbon (roughly $0.4 \leq \frac{SOA}{BC} \leq 1.0$) and POA ($\frac{SOA}{POA} \cong 3.1$) after 5 hours of photo-oxidation [19].

Motivated largely by the health benefits of mitigating diesel PM [23], regulations for HDDV in the U.S. were significantly tightened in 2007, reducing the allowable PM emissions by an order of magnitude and effectively mandating the use of aftertreatment devices (AT) such as diesel particulate filters (DPF). In order to comply with the factor of 10 reduction in nonmethane hydrocarbon (NMHC) and NOx emissions in 2010, HDDVs now also incorporate diesel oxidation catalysts (DOC) and selective catalytic reduction (SCR). Some of these AT technologies are also being implemented in LDDV and MDDV (especially in the EU), and Chirico et al. report that, although primary PM emissions remained unaffected, SOA production was reduced by more than a factor of 20 for LDDV equipped with a diesel oxidation catalyst (DOC). This result is consistent with the well-documented reduction in SOA precursors caused by DOCs [21, 24, 25].

Given the long lifespan of most HDDV, older, higher emitting vehicles are likely to constitute a significant fraction of the HDDV fleet for the next 5-10 years. If in addition to relatively high primary PM emissions (in comparison to gasoline vehicles), these vehicles are responsible for high SOA production, they might be considered low-hanging fruit from a regulatory perspective. One of the aims of this study is to help answer this question by providing some of the first experimental data characterizing SOA production from precursors emitted by HDDV as a function of aftertreatment technology, driving cycle and fuel chemistry.

Although AT technologies have been shown to be highly effective in reducing emissions, one challenge with DPFs is cleaning or "regenerating" the accumulated PM from the filters. Studies have shown that during regeneration both the PM mass and number concentration can increase by orders of magnitude [26]. Furthermore, even during normal (non-regeneration) operation DPFs can emit unexpectedly high concentrations of nucleation mode particles (primarily sulfate) [27]. Given these limitations and the potential to expediently mitigate emissions from older (no AT) vehicles without retrofitting new hardware, it would be advantageous to reformulate fuels to reduce pollutants before they are emitted. Extensive

gasoline reformulation in the 1990s (and earlier) reduced ozone, NOx, CO and air toxics [28]. In connection with these studies, Odum et al. showed that reducing the aromatic content of gasoline reduced the SOA formed when evaporated fuel was photo-oxidized, supporting the conclusion that fuel reformulation may be an effective strategy for reducing SOA precursors from tailpipe emissions.

Combustion emissions are far more complex than vaporized fuel; therefore, the current study investigates the impact of fuel chemistry (using diesels with a range of different aromatic content and a 100% biodiesel) on primary and secondary PM from combustion emissions from 2 MDDV and 3 HDDV from a range of model years and emission standards. In addition, we report the impact of driving cycle (i.e., engine load) on primary and secondary pollutants from vehicles with different aftertreatment technologies (none, DOC, DOC+DPF, DOC+DPF+SCR). Finally, we also characterize the primary and secondary pollutants resulting from DPF regenerations with two different AT technologies (DOC+DPF, DOC+DPF+SCR).

3.3 Materials and Methods

The experimental design for this study, including all combinations of vehicles, fuels, aftertreatment (AT) and driving cycles tested is provided in Figure 3.6 in the SI. Important initial conditions (e.g., NO, NO₂, Δ CO₂, etc.) in all the chamber experiments (including a dynamic blank experiment) are in Table 3.4 of the SI.

3.3.1 Vehicles

Table 3.1 provides highlights some of the important characteristics of the five diesel vehicles used in the smog chamber experiments. The three HDDV (D1, D2 and D3) were owned

by the California Air Resources Board (CARB), and they include one vehicle without AT and two with AT. The two MDDV (D4 and D5) were recruited from the California in-use fleet; D4 had AT and D5 did not. The experiment naming convention is the vehicle ID followed by the experiment number. For example, "D5.3" refers to the 3rd experiment with vehicle 5.

Table 3.1. The three heavy-duty diesel vehicles (D1, D2 and D3) and two medium-duty diesel vehicles (D4 and D5)
used in the smog chamber experiments. The experiment naming convention is based on the vehicle ID. The
complete experimental design matrix is provided in the SI.

	vehicle ID	emissions controls	model year	eng. size (L)	mileage	avg mpg
HDDV	D1	DOC+DPF+ SCR	2010	14.9	11,000	4.5
	D2	DOC+DPF	2007	12.8	22,000	4.9
	D3	none	2006	10.8	94,000	4.3
νd	D4	DOC	2005	6.6	66,000	11.8
MD	D5	none	2001	5.9	159,000	13.7

3.3.2 Fuels

The HDDV were tested with three different ultra-low sulfur diesel (ULSD) fuels: low aromatic (9% aromatic content), mid-aromatic (12% aromatic content) and high aromatic (28% aromatic content). The fuels were analyzed with nitric oxide ionization spectrometry evaluation (NOISE) at a commercial lab specializing in this analysis (Triton Analytics, Houston, TX). NOISE quantifies hydrocarbons by carbon number and hydrogen deficiency [29]. In addition to measuring the mono-, di-, tri-, and tetra-aromatic content, this GC-MS based technique provides weight percentages of 10 other classes of compounds. Basic chemical characteristics of the three ULSD used with D1, D2 and D3 are provided in Table 3.2, and a more detailed analysis is given in Figure 3.11 of the SI. NOISE analysis was not performed with the diesel and biodiesel fuels used in experiments with D4 or D5.

	low aromatic ULSD	mid-aromatic ULSD	high aromatic ULSD
alkanes (%)	19.9	26.4	29.3
cycloalkanes (%)	70.9	61.2	42.7
mono-aromatics (%)	8.8	11.7	23.7
di-aromatics (%)	0.4	0.7	4.2
tri-aromatics (%)	0.0	0.0	0.2
tetra-aromatics (%)	0.0	0.0	0.0
avg # carbons	15.0	14.1	14.7
avg # hydrogens	28.5	27.0	27.2
avg mol wt	208.5	196.7	203.7

Table 3.2. Selected characteristics of the three ULSD fuels used in the HDDV smog chamber experiments. A more detailed chemical analysis is provided in Figure 3.11 of the SI.

In the HDDV experiments fuel was supplied from external tanks (i.e., separate barrels for each fuel type) rather than the vehicles' internal tanks in order to minimize cross-contamination when switching fuels. Each time a different type of fuel was tested with the two DPF-equipped HDDVs a forced regeneration was performed using the new fuel. This regeneration involved ~45 minutes of idle operation, during which time the fuel supply lines were purged. During fuel changes with D3 (no DPF) the recirculating fuel system was rinsed with five gallons of the new fuel while the engine idled, followed by the same 20 minute pre-test warm-up as the other HDDVs.

Both of the MDDV were tested with a commercial ULSD supplied from a local gas station, which was comparable but not identical to the mid-aromatic ULSD used in the HDDV experiments. When D5 was switched from diesel to biodiesel, the vehicle's fuel tank was drained and filled with biodiesel and driven for ~1 hour at 50-60 mph prior to testing.

3.3.3 Driving Cycles

Both MDDV and HDDV were driven on chassis dynamometers following one of the standard certification driving cycles. Important characteristics of all the driving cycles used in this work (and the FTP cycle, which is the main test used for emission certification of light duty vehicles in the U.S.) are shown in Table 3.5 and Figure 3.7 of the SI.

3.3.3.1 Unified Cycle

MDDV followed the cold start Unified Cycle (UC) driving schedule. The UC, which simulates urban stop-and-go driving, has three phases (bags) and a hot soak period: Bag 1 is a 1.2 mile cold start phase lasting 300 seconds; Bag 2 is a 8.6 mile trip phase lasting 1135 seconds; these are run consecutively and followed by a 600 second hot soak (engine off, emissions not sampled); Bag 3 is a hot start phase and duplicates the specifications of Bag 1. The UC is a more aggressive driving cycle than the federal FTP-75, featuring higher average speeds, higher accelerations, fewer stops per mile, and less idle time. Emissions from vehicles operated over the UC are generally higher than when operated over the FTP [30].

3.3.3.2 Urban Dynamometer Driving Schedule

The majority of the HDDV experiments were conducted using the Urban Dynamometer Driving Schedule (UDDS). Following a 20 minute warm-up (10 minutes of driving at 50 mph and a 10 minute hot soak), the UDDS was run two times in immediate succession (to increase the sampling time/resolution), and emissions were collected during the entire 35.4 minute double UDDS cycle; there was no hot soak period between the cycles. While the 2xUDDS differs from the UC used with MDDV (e.g., the maximum speed of the UC is ~15% higher for the UC and sampled idling time for the 2xUDDS is twice as long as the UC), they are both transient cycles. The UDDS represents "typical" urban operation of HDDV, and therefore, we use it to compare MDDV and HDDV. The total sampling time for the UC and the 2xUDDS differ by <5%.

3.3.3.3 Heavy Heavy-Duty Diesel Truck Schedule

In order to assess the impact of low speed driving, one smog chamber test with D3 was performed using a portion of the Heavy Heavy-Duty Diesel Truck (HHDDT) driving schedule [31]. In experiment D3.5 the creep phase of the 4-phase HHDDT cycle (251 s) was run 3 times in immediate succession followed by 1800 s of idling. This cycle differed substantially in several respects from the UC and UDDS (see Table 3.5 and Figure 3.7 of the SI). For example, the 3xcreep+idle was ~25% longer, and the average speed (not including idling) was an order of magnitude lower than the other two cycles.

3.3.3.4 DPF Regeneration

Additional tests were performed with DPF-equipped D1 and D2 to determine the relationship between forced DPF regeneration and SOA production. "Regeneration" refers to the process whereby a DPF is heated >500 °C in order to induce combustion of the PM deposited in the filter during the vehicle's operation. During "forced" regeneration the engine control system initiates combustion of the deposited PM by dosing the DPF with fuel. Although not characterized in these experiments, during normal HDDV operation it is common for the DPF to regenerate passively rather than actively. During passive regeneration the temperature of the emissions is high enough (e.g., when the vehicle is operating at high speeds for an extended time) to cause PM deposited in the DPF to burn spontaneously without any external controls/intervention.

3.3.4 Experimental Setup

MDDV experiments were conducted at the California Air Resources Board's (CARB) Haagen-Smit Laboratory, and HDDV experiments were conducted at CARB's HD Laboratory. Detailed descriptions of these facilities have been published previously [32, 33]. The focus of this report is the smog chamber results, but extensive additional primary only tests were performed with these vehicles and are described in a forthcoming paper [34].

The basic test set-up was the same for both the MDDV and HDDV tests, and a schematic is shown in Figure 3.8 of the SI. The MDDV were driven on a Clayton (Model AC-48) 48" single roll electric chassis dynamometer. HDDV were driven on a Schenck-Pegasus chassis dynamometer powered by a 675 hp D.C. motor. Tail pipe emissions were sampled using Horiba constant volume sampling (CVS) systems at both the HD and the LD labs. A slipstream of the emissions from the CVS were transferred via a 0.5 in o.d. x 12 m long heated (47 °C) Silcosteel (i.e., passivated internal bore) tube into a 7 m³ Teflon smog chamber where they were photochemically aged [35]. Before each experiment the chamber was cleaned by flushing with HEPA- and activated carbon-filtered air overnight. Vehicle emissions were added to an initially half-filled chamber over the entire driving cycle; thus, these experiments represent trip average emissions. The exhaust was diluted in three stages: first, it was diluted 10:1 with ambient temperature HEPA-filtered air in the CVS; it was then diluted 8:1 with 47°C HEPA- and activated carbon-filtered air using Dekati ejector diluters in the transfer line; finally, it was diluted 2:1 in the smog chamber.

Initial PM concentrations inside the chamber ranged from 84-109 μ g/m³ for the HDDV operated on the UDDS (the regeneration and 3xcreep+idle tests had much lower concentrations)

and from 33-165 µg/m³ for the MDDV. The mixing ratios of individual single-ring aromatics in the chamber were typically less than 1 ppb. Initial NOx concentrations were between 0.4 and 1.2 ppm for the HDDVs without SCR and ~0.2 ppm for the HDDV with the SCR. Initial NOx concentrations were between 1.0 and 2.4 ppm for the MDDV. During the MDDV testing the smog chamber was located indoors, in a large air conditioned space; its temperature and humidity varied between 25°C-30°C and 30%-50%. During the HDDV testing the smog chamber was located outside; temperature and humidity in the chamber varied between 19°C-38°C and 9%-51%.

Experiments with D1 and D2 were seeded to mitigate nucleation due to the very low PM emitted by these DPF-equipped HDDV; approximately 10 µg/m³ ammonium sulfate was injected into the chamber just before the vehicle was started. No ammonium sulfate seed was added with the non-DPF-equipped vehicles because the abundant BC in these experiments prevented nucleation. After adding exhaust, nitrous acid (HONO) was bubbled into the chamber as a hydroxyl radical (OH) source, and VOC:NOx ratios were adjusted to approximately 3:1 (typical of many urban environments [36] by adding propene (2.9-3.8 ppm for HDDV and 0.7-4.1 ppm for MDDV). After ~45 minutes of primary characterization, the MDDV emissions were photo-oxidized by exposing them to UV lights (Model F40BL UVA, General Electric); the HDDV emissions were exposed to sunlight continuously for 3 hours.

An array of instruments was used to characterize gas- and particulate-phase pollutants inside the chamber. Particle number distributions were measured with a scanning mobility particle sizer (SMPS, TSI, Inc., classifier model 3080, CPC model 3772). Non-refractory particle mass and chemical composition were measured with a quadrupole Aerosol Mass Spectrometer (AMS, Aerodyne, Inc.). Gas-phase organic species were measured with a proton transfer reaction mass spectrometer (PTR-MS, Ionicon) operated in selected-ion mode with a time resolution of ~2.5 min. The PTR-MS was calibrated daily using a custom gas standard from Spectra Gases. Dedicated gas monitors were used to measure CO₂ (LI-820, Li-Cor Biosciences), SO₂, NOx, CO, and O₃ (API-Teledyne Models 100E, 200A, 300A and 400E); monitors were zeroed daily and calibrated at least weekly. A seven channel aethalometer (Magee Scientific, Model AE-31) measured black carbon (BC), and the aethalometer attenuation measurements were corrected for particle loading effects using the method of Kirchstetter and Novakov [37]. A single particle soot photometer (SP2, DMT, Inc.) was used in parallel with the aethalometer to provide a second, independent BC measurement.

Hydroxyl radical (OH) levels in the chamber were inferred from the decay of VOCs (e.g., toluene, xylenes, TMB, propene) measured with the PTR-MS [38]. Typical experiment average OH levels were 5×10^6 molecules cm⁻³, which is within the range of summer daytime atmospheric concentrations [39]. OH levels were generally higher during the initial stages of the photo-oxidation phase of the experiment and then fell as the HONO was photolyzed.

The primary PM emissions were characterized by collecting filter samples from the CVS using a pre-baked (to remove adsorbed carbonaceous contamination) 47 mm quartz filter and a combined Teflon filter + quartz filter (to correct for sampling artifacts) as described in CFR 1065 [40]. In brief, the pre-baked quartz-fiber filters were collected and analyzed with a Sunset Laboratory Organic Carbon/Elemental Carbon (OC/EC) Analyzer using the IMPROVE protocol [41]. The aethalometer BC measurements were generally higher than the filter EC for the MDDV experiments; thus, while time-resolved BC data were used to calculate wall losses in those experiments, only the (more conservative) EC measurements are reported. The agreement between EC and BC for the HDDV was excellent.

3.3.5 SOA Precursor Measurements

An important objective of this work is to better characterize the precursors that lead to SOA formation. In order to do this we obtained a comprehensive set of organic gas measurements from the CVS.

The measured gas-phase organics are grouped into ten different categories as shown in Table 3.3. The numbers of compounds reported in several of these categories were different for the MDDV and the HDDV because the MDDV emissions were analyzed according to CARB procedures for characterizing emissions from gasoline vehicles. Diesel vehicles emit more high molecular weight compounds than gasoline vehicles, and these compounds are not as readily identifiable by GC-MS; therefore, the number of gas-phase species identified in the low molecular weight VOC category (group 3 in Table 3.3), for example, is 25 for the MDDV (since the emissions from these vehicles were analyzed according to the gasoline vehicle protocol) but only 14 for the HDDV. Five of the ten groups quantify concentrations of individually speciated compounds (groups 2, 3, 5, 7 and 8 in Table 3.3). Two of the groups report lumped sets of compounds that could not be individually identified by the GC but that eluted within a specified time range (groups 4 and 6 in Table 3.3). Group 9 included both speciated data and a co-eluting set of compounds referred to as an unidentified complex mixture (UCM), but for this study these two subcategories within group 9 are lumped together. The FID measurement of THC in group 1 is assumed to include all gas-phase organics except IVOCs and SVOCs, since the latter are higher molecular weight and partition to the particle phase (where they are not seen by the GC-MS) more readily. Group 10 was defined by subtracting from group 1 all speciated and lumped compounds that were assumed to be measured by the FID (i.e., groups 2-8).

Samples from the CVS were collected in heated Tedlar bags and analyzed offline by CARB personnel for total hydrocarbons, methane, light hydrocarbons ($<C_5$), mid-weight hydrocarbons (C_5 to C_{12}) and carbonyls, using standard analytical procedures [42-44]. Briefly, concentrations of speciated C_2 to C_{12} hydrocarbons were determined from two gas chromatographs (GCs): one for analyzing the light-end (C_2 to C_5) hydrocarbons and the second for analyzing the mid-range (C_6 to C_{12}) hydrocarbons. The GCs were equipped with cryogenic pre-concentration (cryotrap) and automated, gas phase sampling valve systems. The light-end GC uses a Varian Al₂O₃/KCl porous layer open tubular (PLOT) analytical column [50 m x 0.32 mm inner diameter (ID)] to separate the hydrocarbon mixture. The mid-range GC uses a Varian DB-1TM analytical column (60 m x 0.32 mm ID, 1 um film thickness). Flame ionization detectors (FID) are used for hydrocarbon detection and quantification. The FIDs are calibrated with a NIST-traceable propane standard.

For the MDDV, 202 different NMOG emission factors were reported. For the HDDV 49 different NMOG emission factors were reported, but additional organic compounds that could not be individually identified by the GC were reported as a function of elution time. These unspeciated compounds were binned according to Kovats index. The fraction of this unspeciated mass with Kovats \geq 800 (i.e., longer elution times and lower volatility than *n*-octane) was assumed to be SOA-forming in subsequent analysis, while the fraction with Kovats < 800 was assumed to non-SOA-forming.

Low-volatility organics in the diluted exhaust were collected using two parallel sample trains of a quartz filter (47 mm, Pall-Gelman, Tissuquartz 2500 QAOUP) followed by two sorbent tubes (Gerstel 6mm OD/4.5mm ID glass tubes filled with 290 mg of a granular porous type of polymer, 2,6-Diphenyl p-phenyleneoxide, called Tenax[™] TA) in series. The inlet line and sample box (filter and sorbent tubes) were maintained at 47°C. The flow rate through each quartz filter was 9.9 liter min⁻¹ and the flow rate through the sorbent tubes was 300 ml min⁻¹. A bypass line was used to exhaust the excess flow downstream of the quartz filter.

Table 3.3. Ten different classes of organic gas-phase compounds characterized in the chamber experiments. The number/type of compounds for both MDDV and HDDV are reported as well as the laboratory techniques used to acquire and quantify the gases.

group	species in group	MDDV	<u>HDDV</u>	sampling method	method of quantification
1	total hydrocarbons	THC	тнс	heated Tedlar bags	heated FID
2	methane	methane	methane	heated Tedlar bags	heated FID
3	low MW VOCs (speciated)	25 compounds	14 compounds	Tedlar bag	GC-MS with a Varian Al ₂ O ₃ /KCl PLOT column
4	low MW VOCs (unspeciated)	0 reported	lumped group, Kovats < 800	Tedlar bag	GC-MS with a Varian Al ₂ O ₃ /KCl PLOT column
5	mid MW VOCs (speciated)	164 compounds	22 compounds	Tedlar bag	GC-MS with a Varian DB- 1™ column
6	mid MW VOCs (unspeciated)	0 reported	lumped group, Kovats ≥800	Tedlar bag	GC-MS with a Varian DB- 1™ column
7	low MW carbonyls	11 compounds	11 compounds	DNPH cartridges	HPLC with a UV detector
8	aromatic carbonyls	2 compounds	2 compounds	DNPH cartridges	HPLC with a UV detector
9	S/IVOCs	lumped group	lumped group	Quartz filter, Tenax tube	TD-GC-MS
10	NMOG balance	lumped group	lumped group	n/a	$group_1 - \sum_{i=2}^{r} group_i$

Filter and sorbent tube samples were analyzed by thermal desorption-gas

chromatography-mass spectrometry (TD-GC-MS). This analysis is described in detail elsewhere [45]; we only briefly outline the method here. The Tenax[™] TA sorbent tubes were cleaned and conditioned via thermal desorption at 320°C under a constant 50 mL/min flow of ultrahigh purity helium. The thermal desorption unit was a Gerstel® TDS3 (Baltimore, MD) system mounted to the inlet of an Agilent 6890 GC and coupled to a mass spectrometer (Agilent 5975 MSD).

Concentrations of individual organic compounds in the quartz filter and TenaxTM TA sorbent samples were determined using multipoint calibration curves developed using authentic standards for a suite of target compounds and a deuterated internal standard to track analyte recovery. The emissions of 62 individual low-volatility organic compounds were quantified, including C_{12} and larger n-alkanes, cyclo- and branched alkanes, naphthalene, substituted naphthalenes, 3-ring polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes. Only a small portion (2.5%) of the total response from quartz filters and TenaxTM sorbent tubes was speciated. The majority of the chromatograms UCM and is not separable with traditional GC techniques. The mass of IVOC for each experiment was determined by multiplying the background-corrected OC (measured with the OC/EC analyzer) by the ratio of IVOC/SVOC, as determined by the TD-GC-MS.

3.3.6 Quantifying SOA Production

To quantify SOA production in the smog chamber we corrected the measured concentrations of suspended particles for (a) the loss of organic particles and vapors to the chamber walls, (b) the increase in the particle loss rate for experiments in which nucleation occurs, and (c) the lower particle detection efficiency by the aerosol mass spectrometer (AMS) for particles smaller than about 60 nm. Wall loss corrections (a) are important in every experiment, whereas corrections for (b) and (c) are significant only in a few experiments (e.g., as a result of particle nucleation during DPF regeneration when chamber concentrations were dominated by smaller particles). Correction (a) is described below; corrections (b) and (c) are described in the SI. Organic particles and vapors are lost to the chamber walls as a function of time, and total OA is the sum of the measured (via the AMS) suspended mass plus the mass of organics on the chamber walls

$$OA_{total,t} = OA_{sus,t} + OA_{wall,t}$$
⁽⁵⁾

Organics may be lost to the chamber walls as particles or vapors. Loss of organic particles is treated as a first-order process [46] with a rate constant determined from the decay of BC measured by the aethalometer

$$C(t) = C_0 e^{kt}$$

where *C* is the BC concentration at time *t*, C_o is the initial BC concentration and *k* is the wall loss rate constant. The wall loss rate constant depends on the size and composition of the particles, turbulence in the chamber, the size and shape of the chamber, and particle charge [47]. Therefore, it was determined for each experiment by fitting each time series of BC data. Aethalometer measurements can be influenced by particle coating [48]; therefore, a single particle soot photometer (SP2, DMT, Inc.) was used in parallel with the aethalometer to quantify BC, and the two instruments showed excellent agreement: average difference between the wall loss rates calculated from the aethalometer and the SP2 was 4% (n=8). The particle wall loss rate for MDDV experiments ranged from -0.570 to -0.655 hr⁻¹ (i.e., after approximately 1.5 hr the BC concentration decreased to 37% of its initial value). Wall loss rates for the HDDV without AT varied between -0.460 to -0.530 hr⁻¹ for different experiments. For experiments without enough BC to calculate a rate constant the decay of sulfate seed particles was used. In two experiments (D2.12 and D2.8) there was not enough BC or sulfate, and an average rate constant from the other experiments was used instead. Using BC as a tracer for wall loss assumes that it is internally mixed with the OA. This assumption was valid for most experiments because the size resolved data (SMPS and AMS) only showed growth of the primary mode aerosol. However, the majority of particle mass in the two regeneration experiments was formed from nucleation. Therefore, in these experiments it was necessary to adjust the wall loss rate to account for the more rapid loss of smaller nucleation mode particles. This correction is discussed in the SI.

The loss of condensable organic vapors to wall-bound particles is constrained by considering two limiting cases: the first (Method #1) assumes that no organic vapors condense to wall-bound particles, and the second (Method #2) assumes that organic vapors remain in equilibrium with both wall-bound and suspended particles. The loss of organic vapors directly to the chamber walls (in distinction to their loss to wall-bound particles) is highly uncertain, and in keeping with virtually every other chamber study in the literature, we do not account for it here. If it were included, it would *increase* our estimate of SOA production.

Method #1 provides a lower bound estimate of the SOA mass production; it is equivalent to the " $\omega = 0$ " correction utilized in previous studies [22, 49]. Method #1 assumes that mass transfer resistance to the walls is much greater than to the suspended particles. This is a reasonable assumption since condensable vapors are in continuous, intimate contact with suspended particles, whereas their interaction with wall-bound particles is likely to be far less frequent. A consequence of this wall loss assumption is that suspended and wall-bound particles may have different compositions.

Assuming no loss of vapors to the walls in Method #1, the rate at which OA mass is lost to the chamber walls is
$$\frac{d}{dt}(OA_{wall}) = OA_{sus}(-k) \tag{6}$$

where OA_{sus} is the AMS-measured (i.e., suspended) OA mass at time *t* and *k* is the negative wall loss rate constant of black carbon [22]. The total OA in the chamber is calculated by numerically integrating equation (2) and adding the calculated OA lost to the wall to the measured OA concentration (equation (1)).

Method #2 assumes that particles lost to the walls during an experiment remain in equilibrium with the vapor phase. This case corresponds to the " $\omega = 1$ " correction [22]. The total OA mass at time *t* is equal to the suspended particle mass scaled by the ratio of the initial black carbon concentration to the black carbon concentration at time *t*

$$OA_{total,t} = OA_{sus,t} \cdot \frac{C_0}{C_t} \tag{7}$$

where C_o is the initial black carbon concentration and C_t is the measured black carbon concentration at time *t*. As only *suspended* OA is referenced in equation (7), the PM on the wall and in suspension has the same composition.

In experiments with low BC concentrations, the total OA estimates from Method #2 can be noisy due to their inverse dependence on BC in (7). For such experiments, we implemented Method #2 using the previously described exponential fit to the BC data rather than the actual BC data themselves,

$$OA_{total,t} = \frac{OA_{sus,t}}{e^{kt}} \tag{8}$$

where *k* is the negative wall loss rate constant of black carbon.

Experiments of Weitkamp et al. [22] indicate that the rate of vapor uptake to particles on the walls is the same as the rate for suspended particles (Method #2), suggesting that the mass

transfer resistance of organic vapors to wall-bound particles is comparable with that to suspended particles. Equations (7) and (8) indicate that in Method #2 the loss of organic vapors to particles on the walls scales with the mass fraction of particles on the walls to particles in suspension. Initially (before any particle loss) there is no loss of vapors to wall but it increases as an experiment progresses. Therefore, estimates based on Method #1 and #2 diverge as more particles are lost to the wall, and the uncertainty in the observed SOA production increases as an experiment progress [50]. Given this increasing uncertainty, we imposed a 5:1 upper bound on the ratio of OA on the wall to suspended OA. This condition was binding in roughly half the experiments, and when it was binding, it was typically only later in the experiment after 1.5-2.5 hours of photo-oxidation. The average and range of OA from Methods #1 and #2 is reported in the results.

Chamber blank experiments performed after filling the chamber with CVS dilution air, HONO, and ammonium sulfate seed particles produced 1-3 μ g/m³ of SOA over a 3 hour photooxidation period. This SOA is likely formed from the residual vapors that desorb from the CVS, transfer line and chamber wall. Therefore, for every chamber experiment we assume an SOA blank of 0 μ g/m³ at t=0 that increases linearly to 2 μ g/m³ of SOA at t=3 h and subtract this artifact from the reported SOA production.

3.3.7 Repeatability

Duplicate experiments were performed with all three of the HDDV with each of the three fuels to quantify the repeatability of the measurements. There is a small amount of variability in both the emissions from the vehicles and in the propene spiking to adjust VOC/NOX. In duplicate experiments with D3 NMOG differed by <5%, POA<10%, BC<3% and SOA<40%.

While a 40% difference in SOA between duplicate experiments may appear to be rather large, part of the difference is likely due to differences in gas/particle partitioning in different experiments. Furthermore, the 40% difference in SOA is based on comparisons of experiments with different fuel types, and it may, therefore, be the slight differences in fuels rather than experimental variability that is responsible for the observed differences in SOA with D3. Repeatability with D1 and D2 was excellent; primary gas- and particle phase emissions and SOA production were consistently equal to zero, as is discussed in conjunction with Figure 3.2Figure 3.3 in the Results and Discussion section.

Repeatability with the MDDV experiments was also good, but this was not tested as extensively as with the HDDV. In duplicate experiments with D4 using biodiesel the primary gas and particle emissions differed by <10%; the SOA differed more, but this is due to the fact that the photo-oxidation period in one experiment was twice as long.

3.3.8 Data Analysis

Pollutants are reported per mass of fuel burned (mg pollutant / kg fuel):

$$EF = \frac{[P]}{[CO_2]} \cdot \frac{MW_{CO2}}{MW_C} \cdot C_f \tag{1}$$

where *[P]* is the background corrected pollutant concentration in $\mu g/m^3$, *[CO2]* is the background corrected concentration of CO₂ in the chamber in $\mu g/m^3$, MW_{CO2} is the molecular weight of CO₂ (44.1 g/mol), MW_C is the molecular weight of carbon (12 g/mol) and C_f is the carbon intensity of the fuel determined from fuel analyses (0.85 kg-C/kg-fuel for diesel, 0.77 kg-C/kg-fuel for biodiesel). This analysis assumes that all carbon in the fuel is converted to CO₂, which introduces negligible error in our analysis.

The fragmentation table from Allan et al. [51] was used to interpret AMS data. The contribution of gas-phase CO₂ to the AMS m/z 44 signal was corrected using the measured CO₂ concentrations. CO₂ levels in the chamber after exhaust injection ranged from 493 to 764 ppm for the HDDV and 574 to 618 ppm for the MDDV tests. There was no evidence of organic particle signal at m/z 28 (CO⁺). Organic and inorganic nitrates fragment into NO⁺ and NO₂⁺ in the AMS, but organic nitrates generally have a considerably higher ratio of NO⁺ to NO₂⁺, making it possible to apportion nitrate signal between the two classes. Using the approach of Farmer et al. [52], only a minor fraction (typically <5%) of the nitrate mass (which was usually quite small) was attributable to organics.

3.4 Results and Discussion

3.4.1 Time Series of Typical Smog Chamber Experiment

Figure 3.1 illustrates the temporal evolution of both particle- and gas-phase species during a typical smog chamber experiment (experiment D3.13). There are three distinct periods in each experiment. First, vehicle emissions are added to the chamber throughout the entire driving cycle (the 35 minute 2xUDDS is shown here), increasing the concentrations of VOCs, CO_2 and NOx. The second period begins when the engine was shut off at time = -2 hours. The primary emissions were characterized during this period, and HONO was added to the chamber at approximately time = -0.5 hours, leading to a modest increase in NO₂ concentration. Propene was also added to adjust the VOC/NOx ratio to approximately 3. The loss of POA to the walls of the chamber is evident from the decay of the organic signal (blue line in Figure 3.1c) occurring between the time when the engine is turned off and before the chamber is exposed to

UV at time = 0 hours. The third period begins when the UV lights were turned on (MDDV) or the chamber was exposed to sunlight (HDDV). SOA was quickly generated at the beginning of this period, while the wall-loss corrected black carbon concentration (red line in Figure 3.1c) remained constant. After 3 hours the wall-loss corrected organic concentrations increased by roughly a factor of 3 from ~7 μ g/m³ of POA to ~26 μ g/m³ of OA (average of the ω =0 and ω =1 estimates in Figure 3.1c). During the 3 hours of UV irradiation much of the NO and primary hydrocarbons are oxidized to NO₂ and oxygenated VOCs, respectively (Figure 3.1a-b).



Figure 3.1. Gas and particle evolution during a typical smog chamber experiment (D3.13). Between -2.5 hr < time < -2.0 hr, the chamber was filled with dilute emissions from the vehicle; for -2.0 hr < time < 0 hr, the primary PM was

characterized; for time > 0 hr, the UV lights were on and photo-oxidation generated SOA. Concentrations of NOx, O_3 and CO_2 are shown in (a). Shown in (b) are the concentrations of two VOCs which are consumed by OH radicals. Shown in (c) are uncorrected and corrected (for wall losses) organic PM and black carbon concentrations; the large increase in organic PM mass is due to SOA production. The organic concentrations were corrected using two different methods (ω =0 and ω =1) which provide an estimate of the uncertainty of the SOA production. The discontinuity at about t=0 for the uncorrected BC is an artifact of the aethalometer tape advance. The OA (ω =1) is capped at about t=2.6 hr when wall OA/suspended OA =5.

3.4.2 Impact of Aftertreatment

Data for BC, POA and SOA mass per kg of fuel burned for light- and heavy-duty diesel vehicles are shown in Figure 3.2. The data are for end of experiment, after ~3 hr of photo-oxidation, which generated an OH exposure of $1-2x10^7$ molec-hr cm⁻³. This corresponds to 3.5-7 hrs of equivalent atmospheric aging at typical summertime OH concentrations of $3x10^6$ molec cm⁻³. Data denoted with an asterisk are from Chirico et al. [19].



Figure 3.2. Chamber measurements of black carbon, POA and SOA from light- and heavy-duty diesel vehicles. Average values from 15 medium-duty gasoline vehicles (MY1987 through MY2011, experiments described in a companion study) are included on the right side for comparison. The three sets of data denoted with an asterisk are taken from Chirico et al. [19]. Data for the three vehicles denoted by the \ddagger symbol are averages (error bars are $\pm 1\sigma$) for all the UDDS tests with each of those vehicles, including experiments utilizing different types of fuel. Data shown for D5.3, D4.1 and D3.5 represent a single experiment from each vehicle and the error bars denote the SOA range obtained by applying the ω =0 and ω =1 wall loss correction approaches. The inset presents the LDGV data at a factor of 10 higher resolution.

The most striking finding in Figure 3.2 is the dramatic reduction in all aerosol species for DPF+DOC-equipped vehicles. BC and POA emissions and SOA formation in the chamber were all below the detection limit (~10 mg/kg-fuel) for the two HDDVs with DPFs (D1 and D2). The DPF+DOC aftertreatment system is also highly effective in mitigating PM from MDDVs as indicated by the very low levels of all aerosol species measured during the "2001 DOC+DPF" experiment (Figure 3.2). In comparison to the order of magnitude or greater reduction in PM between DPF-equipped and non-DPF equipped vehicles, differences between the non-DPF equipped vehicles—both the MDDV and the HDDV—were much less pronounced. For example, D3 ("D3 avg UDDS" in Figure 3.2) emitted roughly one half to one third as much POA as D5.3 and one of the DOC-equipped MDDV ("2002 DOC"), respectively (50 mg/kg vs. 80 mg/kg and 130 mg/kg), and BC levels were roughly comparable across these same experiments. Although qualitatively similar, BC and POA emissions and SOA formation for D4 differed somewhat more from the other non-DPF equipped vehicles, but there is a very clear distinction between the extremely low levels of BC and POA emissions and SOA formation for DPF+DOCequipped vehicles compared with the levels measured in experiments with vehicles with no AT or with only a DOC.

The data shown in Figure 3.2 indicate that DOCs reduce SOA: more SOA was generated during the two MDDV experiments without AT (D5.3 and 2000) than the two MDDV experiments with DOCs (D4.1 and 2002). This result is consistent with Chirico et al. who report (data not shown) a substantial reduction in SOA using a single MDDV with and without a DOC; the DOC had no effect on POA [19]. We would anticipate that the observed SOA reduction would be reflected in a reduction in NMOG, since some NMOG emissions are SOA precursors. However, Figure 3.3a indicates that the total NMOGs for D4.1 (~1000 mg/kg-fuel, DOC) are

slightly greater than those of D5.3 (~700 mg/kg-fuel, no DOC). This suggests either that the DOC was malfunctioning in D4.1 or that the higher SOA production of D5.3 could be due to a larger fraction (or a higher yielding mix) of unspeciated NMOG. The current study cannot identify the correct explanation because instrument problems made it impossible to determine the unspeciated NMOG for D4 (Figure 3.3b). As a result, the unspeciated NMOG value was set to zero for D4.1 in Figure 3.3b.



Figure 3.3. (a) POA, SOA and total non-methane organic gases from light- and heavy-duty diesel vehicles with a range of different fuels (D=commercial ULSD, BD=100% soy biodiesel, H=high aromatic ULSD, M=mid aromatic ULSD, L=low aromatic ULSD), and driving cycles (UC for MDDV, UDDS and creep for HDDV). Data for two of the vehicles—D1 and D2—are averages (error bars are $\pm 1\sigma$) for all the UDDS tests with each of those vehicles, including experiments utilizing different types of fuel. Bars shown for the D3, D4 and D5 are from individual experiments with each vehicle, and these error bars denote the SOA range obtained by applying the ω =0 and ω =1 wall loss correction approaches. (b) Total NMOG shown in (a) is divided into SOA precursors (groups 5, 6, 8 and 9

from Table 3.3), non-precursors (groups 2, 3, 4 and 7 from Table 3.3) and NMOG balance (group 10 from Table 3.3). SOA precursors include single-ring aromatics, mid-weight VOCs (Kovats index \geq 800), SVOCs and IVOCs. Non-precursors include non-aromatic lightweight VOCs (Kovats index<800). The unspeciated mass was determined by subtracting all the speciated NMOGs and the S/IVOCs from the total NMOG measurement (see table in SI). The bullet (•) symbol for D5.1 and D5.2 (both with BD fuel), D4.2, and D3.9 experiments indicates that no data are available for the NMOG composition. The § symbol for the D1 and D2 experiments indicate that there is no fractional composition data for these experiments because the NMOG was zero for the two HDDV with aftertreatment.

Many previous studies have reported >90% reductions in primary PM from both heavyduty [32, 53, 54] and medium-duty [55, 56] DPF-equipped diesel engines. However, comparatively little has been published on the effect of aftertreatment on SOA formation. Samy and Zielinska also report very low organic vapor emissions and subsequent SOA formation from a DOC-equipped diesel engine [21]. In their experiments it was necessary to add a large amount of exogenous VOCs to the engine emissions to enhance their reactivity (and to better simulate urban conditions) sufficiently to make even modest amount of SOA (<50% of final particle mass in chamber).

Average BC, POA and SOA values from experiments with 15 different medium-duty gasoline vehicles (MY1987 through MY2011) are also included on the right side of Figure 3.2 [57]. As expected, BC for the gasoline vehicles is much lower than any of the non-DPF equipped diesels. However, POA and SOA for gasoline vehicles and non-DPF equipped diesel vehicles are closer. In particular, SOA formation appears to be roughly comparable for DOC-equipped MDDV and gasoline vehicles.

It is important to note that comparing our study with the one by Chirico et al. as we do in Figure 3.2 is complicated somewhat by at least two significant differences in experimental approach. First, in the current study standard driving cycles were used, so the measured emissions profiles are expected to provide a reasonable simulation of those found widely on the roads; however, vehicles in the study by Chirico et al. were either operated at idle or at a constant 60 km/h, presumably making their measurements somewhat less reliable models of real world conditions. Second, we report SOA after 3 hours of photo-oxidation while their SOA values are after 5 hours. We expect that the amount of SOA generated in our experiments would continue to increase modestly over the additional 2 hours.

3.4.3 Impact of Driving Cycle

3.4.3.1 Creep+idle vs. UDDS

At low engine load conditions characteristic of the 3xcreep+idle test cycle ("D3.5 creep" in Figure 3.2), BC emissions are reduced and SOA increased substantially relative to the "D3" tests using the UDDS cycle. This reduction in BC is consistent with many other studies using a variety of engines [58-60] that have shown that OC/EC ratio is inversely related to engine load. Additional experiments (data not shown) in which only the primary emissions are characterized [34] show that NMOG emissions are also higher with D1 and D2 during 3xcreep+idle tests than during UDDS (130 mg/kg-fuel and 3500 g/kg, respectively) despite the fact that they both have DOCs. Compared to ~6.2 g/kg from D3, D1's NMOG emissions are very low (although still above the detection limit). NMOG emissions from D2 during 3xcreep+idle are more than half as large as those from D3 during 3xcreep+idle, suggesting that a significant amount of SOA may be produced under low load driving conditions for DPF-equipped vehicles (D1 and D2), but smog chamber experiments were not performed to verify this.

3.4.3.2 DPF Regeneration

Emissions from D1 and D2 generated during forced DPF regenerations were photooxidized in the smog chamber in experiments D1.15 and D2.18. Figure 3.5 shows that POA emissions during regeneration were comparable to that measured during UDDS tests with D3, but BC emissions were much lower (0.02 g/kg-fuel vs. 0.58 g/kg-fuel for the D1 and D3, respectively).

A distinguishing feature of regeneration (compared to UDDS or creep) was the emission of a large quantity (0.2 g/kg-fuel to 0.4 g/kg-fuel) of sulfate particles. Other researchers have reported nucleation-enhanced emissions during DPF regeneration with HDDV [61] and LDDV [62]. Several studies report that sulfate is an important nucleating species during DPF regeneration even when ultra-low sulfur diesel is used [63, 64]. Although regeneration does increase particle mass emissions (and greatly increases number concentrations), Guo et al. claim that the overall efficiency (including the estimated duty cycle of regeneration/normal operation) of the DPF exceeds 97% even with high sulfur fuel [64].

Photo-oxidation of the dilute forced regeneration emissions in the smog chamber produced significant SOA. These were the only experiments with the DPF-equipped vehicles in which SOA was formed—0.04 g/kg-fuel and 0.1 g/kg-fuel for D1 and D2, respectively. This SOA formation was associated with NMOG emissions from both D1 and D2. D2 emitted a significant amount of NMOG (~130 mg/kg-fuel) during the regeneration experiment. Although D2's NMOG emissions during regeneration are an order of magnitude lower than during the 2xUDDS tests with the non-AT vehicle (D3 average = 1260 mg/kg-fuel), the amount of SOA produced during D2's regeneration is 1-2 greater than what is produced by D3 during UDDS. A smaller amount (8 mg/kg-fuel) of NMOG was emitted during the D1 regeneration.

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3.4.4 Impact of Fuel Chemistry and Experimental Repeatability

Figure 3.3 presents the gas- and particle-phase data for the experiments in Figure 3.2 (excluding the data from Chirico et al.) broken down by differences in fuel chemistry and expanded to show experimental repeatability. (Experiments with the two DPF-equipped HDDVs, D1 and D2, are not differentiated by fuel because emissions in every case were below the detectible limit regardless of fuel type.) For example, instead of a single stacked bar for vehicle D5 (MDDV, no AT) as in Figure 3.2, there are three stacked bars in Figure 3.3a, corresponding to the three experiments with this vehicle, including two different fuels and a duplicate experiment. Figure 3.3b shows the distribution of NMOG broken into SOA precursors, non-precursors and unspeciated (see SI).

A major finding of this study is that POA, NMOG emissions and SOA production were independent of the aromaticity of the fuel. Although gas phase measurements in the chamber do indicate a positive correlation between fuel aromaticity and aromaticity of combustion emissions (see Figure 3.10 in SI), Figure 3.3a-b indicate no systematic effect of fuel on POA or SOA amounts. This is true for both the DPF-equipped HDDVs (D1 and D2), where no PM was produced with any of the fuels when driven over the UDDS, and for D3, where the POA and SOA were identical for four of the five experiments using the three different fuels. BC measurements for D3 from the five experiments were also tightly grouped with no distinguishable trend based on fuel type (average $\pm 1\sigma$ shown in Figure 3.2; individual values not shown). Furthermore, the relative amounts of NMOG (Figure 3.3b) in the different categories (SOA precursor, non-precursor and unspeciated) are also identical for the D3 experiments (UDDS cycle) regardless of fuel type. The NMOG data for the DPF-equipped HDDV are all below detection limit so we cannot draw any conclusions about potential fuel effects.

One of the MDDV (D5) was tested with both commercial ULSD and biodiesel. Although there was no effect on POA emissions, EC emissions were reduced significantly with biodiesel (data not shown), which is consistent with many studies [65] and references therein that report a 40-75% reduction in (primary) PM emissions when replacing diesel with biodiesel. More data are required to determine conclusively biodiesel's impact on SOA formation. For the base experiment (VOC/NOx ~3) there does not appear to be a significant effect. When the biodiesel experiment was repeated at a significantly lower VOC/NOx ratio (=0.7 vs. 3.8 in the base experiment) the EC and POA levels remained constant, while the SOA production was reduced by more than a factor of 2 (experiments D5.2 and D5.1, respectively). This is assumed to be due to the fact that under high-NOx conditions NO and NO₂ react with organo-peroxy radicals (RO₂), which changes the distribution (and volatilities) of oxidation products, reducing SOA yields. Other researchers have shown that SOA production is reduced in single component smog chamber studies when VOC/NOx is reduced [66, 67].

Figure 3.3 demonstrates the good repeatability of these experiments, especially with the HDDV. The duplicate HDDV experiments with high aromatic fuel ("H") have nearly identical emissions profiles; this is also true of the low aromatic fuel duplicates. The duplicate MDDV experiments labeled "D" produced comparable amounts of SOA and NMOG, but their POA emissions differed. POA emissions from the two MDDV experiments labeled "BD" were nearly identical. The moderate difference in SOA production for these two experiments is likely due to the fact that they were not truly duplicates: the experiment with the lower SOA was stopped after only 1.5 hr of photo-oxidation rather than 3 hr for the other BD experiment.

3.4.5 Effective SOA Yields

To investigate the effect of NMOG emissions on SOA production, the SOA mass after 3 hours of photo-oxidation was compared to the estimated mass of reacted SOA precursors. The ratio of these quantities provides an estimate of the effective SOA yield. For speciated compounds, the reacted mass was calculated from the measured initial concentration, the estimated OH exposure and the reaction rate constant from the literature. We considered four different SOA yield cases, using a different subset of the NMOG for each (see SI for further information on species included in each SOA yield case):

- 5. Case 1 (traditional SOA model)— groups 5, 6 and 8 in Table 3.3, which includes known SOA precursors: single-ring aromatics (C₆ to C₁₂) and mid-weight VOCs (e.g., *n*-alkanes and other species with Kovats \geq 800), a part of which was comprised by a lumped group of compounds that could not be individually identified by the GC but that eluted with mid-molecular weight VOCs. An OH reaction rate of 1.67×10^{-11} cm³ molecule⁻¹ sec⁻¹ was assumed for the lumped group; this was the average OH rate constant for the speciated mid-molecular weight VOCs.
- 6. Case 2—precursors in case 1 + SVOCs and IVOCs (group 9 in Table 3.3). Unspeciated S/IVOCs were lumped together and assumed to react at 3x10⁻¹¹ cm³ molecule⁻¹ sec⁻¹. This value is an extrapolated average for reaction rates of C₁₂ and larger organics.
- 7. Case 3—precursors in case 2 + the NMOG balance (group 10 in Table 3.3), which was assumed to react at 1×10^{-11} cm³ molecule⁻¹ sec⁻¹.
- 8. Case 4—precursors in case 3 + all remaining NMOGs (groups 3, 4 and 7 in Table 3.3), including compounds that are unlikely to be SOA precursors (e.g., all non-aromatic

compounds with Kovats numbers < 800). A fraction of this precursor mass was comprised by a lumped group of compounds that could not be individually identified by the GC but that eluted with the low molecular weight VOCs. Reaction rates were taken from published measurements or models, except for the lumped group, which used the average OH rate constant $(2.79 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})$ for the other low molecular weight VOCs.

Cases 1-4 span the range of conceivable SOA precursors—from the limited set of traditional compounds to the complete mass of all organic vapors. In some experiments a significant fraction (average for all experiments was ~30%) of the NMOGs were unspeciated, including some oxygenated compounds (which may be underestimated by flame ionization detectors [68]), and case 3 examines the effect of including them in the calculation of SOA yields. Case 3 is assumed to be the best estimate. Case 4 provides a lower bound of the SOA yield by including everything, even the compounds that are known to be non-SOA precursors (e.g., ethane, acetone, etc.). While some of these compounds react too slowly with OH to be SOA precursors (e.g., the OH reaction rate for ethyne is 8.2×10^{-13} cm³ molecule⁻¹ sec⁻¹), even those which react quickly (e.g., the OH reaction rate for2-methyl-1,3-butadiene is 1.8×10^{-10} cm³ molecule⁻¹ sec⁻¹) are so volatile that they are unlikely to partition to the particle-phase even after several generations of chemical transformation.

The four yield cases for each of the five D3 experiments are shown in Figure 3.4, and on the right side are the average yields $\pm 1\sigma$ for seven experiments with five different gasoline vehicles. If only traditional precursors form SOA (case 1), then the estimated yields are 20-75%. This is unrealistically high. As a point of comparison, single compound chamber studies have reported a wide range of SOA yields, but they are generally much lower than 75%. For example, SOA yields for toluene ranged from 11-49% (COA=10 μ g m⁻³) [50] under a variety of experimental conditions, but earlier toluene studies [69, 70] reported yields that were an order of magnitude lower. Odum et al. reported yields from whole gasoline vapors—a more complex system (and therefore presumably closer to combustion emissions) than single compounds—that range from about 2-5% at (COA≈10 μ g m-3) [71]. Compared to these studies, case 1 yields are unrealistically high, indicating that additional precursors are required for mass closure.

Other studies have also demonstrated that traditional SOA precursors do not explain the amount of SOA formed from the photo-oxidation of combustion products of various fuels, including wood, diesel and jet fuel [22, 49, 72]. Even after increasing the SOA yields of traditional precursors to reflect the most recent literature values, Robinson et al. found that these precursors were only able to account for one quarter or less of the measured SOA from wood smoke and diesel fuel [73]. In addition to these chamber studies many ambient studies have shown that local, regional and global scale computer models systematically underpredict the measured ambient SOA when parameterized by only traditional SOA precursors [6-8].

Robinson et al. argued that SVOCs and IVOCs are responsible for substantial SOA production [74], and that by including them in model parameterizations, it may be possible to improve predictions relative to measured ambient conditions. Indeed, studies have shown that models which incorporate these non-traditional SOA precursors have been more successful in predicting observed SOA concentrations in the atmosphere [75-77]. However, it is experimentally challenging to fully quantify these lower volatility compounds. In this study they were measured with quartz filters and Tenax followed by TD-GC-MS analysis. But it is likely

that some of the SVOC and IVOC emissions are not being characterized using these operationally defined methods.

As more precursors are added to the analysis (cases 2 through 4), the effective SOA yields decrease. For example, Figure 3.4 shows that incorporating the S/IVOCs in the yield estimate (Case 2) reduces the yields only slightly from 20-75% to 10-35%. Including the unspeciated NMOGs (in Case 3, the best estimates) reduces yields by an additional factor of two from 4-19%. The yields are reduced further in Case 4 but not as dramatically as in the other cases. Overall Case 3 provides a plausible explanation for the observed SOA production in the D3 HDDV experiment, and these yields are somewhat lower than the average yield from the 7 gasoline experiments.



Figure 3.4. SOA yields from D3 (HDDV with no AT) and the average SOA yield for 7 different medium-duty gasoline experiments (5 unique vehicles). Bars indicate best estimates. For the gasoline vehicle averages, the upper limit of the error bars assumes the chamber blank=0 μ g/m³, wall loss correction Method #2 (high SOA estimate) and reduces the available S/IVOC mass by a factor of 3. The lower limit of the error bars assumes the chamber blank=5 μ g/m³ (at t = 3 hr) wall loss correction Method #1 (low SOA estimate) and increases the available S/IVOC mass by a factor of 3. The species used to create the four different cases are presented in the SI.



Figure 3.5. Primary PM emissions and SOA formed from diesel particulate filter (DPF) regeneration. The BC, POA, SOA and sulfate for two control (i.e., UDDS, non-regeneration) experiments are shown to the right of each of the two regeneration experiments (one regeneration experiment for each of the two HDDV with DPFs). For each vehicle the two control experiments and the regeneration used the same fuel (low aromatic with the D1 and mid-aromatic for D2). On the far right are the average values (error bars are $\pm 1\sigma$) for all the UDDS tests with D3, which did not have a DPF or other aftertreatment, including experiments utilizing different types of fuel. Error bars for the regeneration experiments denote the SOA range obtained by applying the $\omega=0$ and $\omega=1$ wall loss correction approaches.

3.5 Conclusions

The effects of photochemical aging on dilute emissions from two medium-duty diesel vehicles and three heavy-duty diesel vehicles were investigated to improve our understanding of how emissions from the tailpipe transform in the ambient atmosphere. Vehicles with a range of emission controls were tested with five different fuels and four different driving cycles. In contrast to uncontrolled (i.e., no DPF) diesel vehicles which emitted high concentrations of BC and modest amounts of POA, DPF-equipped vehicles emit essentially no primary PM (BC or organics) during normal urban driving.

For both MDDV and HDDV without aftertreatment substantial SOA formed when their emissions were photo-oxidized in the smog chamber for three hours —with the emissions from some vehicles generating twice as much SOA as POA after three hours of oxidation at typical urban VOC/NOx ratios. Although SOA production from diesel- and biodiesel-fueled vehicles without a DPF was significant on an absolute basis, the net PM from these vehicles was dominated by BC. For the HDDV without a DPF the SOA yield (estimated from the calculated oxidation of speciated non-methane organic precursor gases) was approximately 10%. While net PM (primary+secondary) and POA were comparable for slow/idle (i.e., the 3xcreep+idle driving cycle) and high speed urban operation (i.e., the UDDS cycle), SOA production from slow/idle operation was 3-4 times larger than SOA production from the UDDS cycle. This appears to be due to the much higher concentrations of NMOG emitted during the slow/idle operation. Reduced BC emissions partially offset the increased SOA production during the slow/idle tests. For one of the MDDV, switching from ULSD to biodiesel reduced BC substantially, but POA and SOA were unchanged.

The aromatic content of the three different test fuels used in HDDV tests had no effect on the amount of primary PM emissions or secondary PM production. The fact that fuel aromaticity was independent of SOA production in this study underscores the strong distinction between photo-oxidation of actual vehicle emissions versus vaporized fuel. In contrast to this study, Odum et al. found that fuel aromaticity nearly perfectly predicted SOA yields when vaporized fuel was photo-oxidized [71]. Our results indicate that reformulating diesel by altering aromatic content alone is not likely to have a significant impact on either primary or secondary PM. Driving cycle, on the other hand, has a large impact on SOA production, and expanding or optimizing existing efforts to limit truck idling may be a more attractive control strategy. Indeed, regulations establishing idling limits have already been adopted in certain states. For example, in 2008 California imposed restrictions on idling trucks with gross weights >10,000 pound [78], limiting them to 5 minutes of idling under many circumstances. Currently there is no federal anti-idling regulation, and only about half of the U.S. regulates idling.

Photo-oxidized gas-phase emissions from DPF-equipped vehicles produce nearly zero SOA during normal urban operation; however, non-negligible amounts of SOA, BC, POA and sulfate were measured during forced DPF regeneration experiments. Therefore, it is important to estimate regeneration's impact on SOA production relative to SOA produced from emissions from an uncontrolled HDDV. As part of a recent report on the health effects of long term exposure to diesel emissions, the frequency and duration of DPF regeneration was studied extensively [79]. Based on that report we estimate that a DPF-equipped HDDV passively regenerates its DPF during 17% of the miles traveled. In our experiments the SOA production during active regeneration was 0.09 g SOA/kg fuel, and SOA production for the uncontrolled HDDV was 0.1 g SOA/kg fuel. Neglecting potential differences in active and passive regeneration (due to a lack of data) and assuming that SOA production for the DPF-equipped vehicle is zero during non-regeneration operation, we estimate that the ratio of SOA from a DPFequipped vehicle to SOA from an uncontrolled vehicle is

$$\frac{0.17 \times 0.09 \ g \ SOA/kg \ fuel}{0.1 \ g \ SOA/kg \ fuel} = 0.153 \tag{9}$$

This is a zeroth order estimate, incorporating some major assumptions. Nevertheless, if DPFequipped HDDV produce on the order of 15% as much SOA as uncontrolled HDDV as indicated by Equation (9), further study may be warranted in order to better constrain total PM production from DPF-equipped HDDV.

3.6 References

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3.7 Supplementary Information

Table 3.4. Initial conditions in the chamber for all experiments with HDDV, MDDV and a dynamic blank (blank used air from the CVS, but no vehicle exhaust).

	test date	exnt ID	model vear	emiss.	fuel	driving cycle	VOC/	seed?	mng	PM _{t=0}	POA	BC (ug/m ³)	∆CO₂ (nnm)	NO (ppb)	NO ₂	propene (ppm)	NMOG (nnmC)
	- / /	captib	yeu	control		unting cycle	NOX	Jeeu.	11125	(P6/ 11 /	(146/111/	(P6//	(PP)	(666)	(666)	(pp)	(ppine)
Î	7/11/2011	D1.1	2010	^a DOC, DPF, SCR	28% arom. ULSD	2xUDDS	3.07	Y	4.41	1.9	0.3	0.6	354	170	376	0.60	0.41
	7/12/2011	D1.4			28% arom. ULSD	2xUDDS	2.98	Y	4.48	4.8	0.6	0.6	258	200	389	0.60	0.00
	7/13/2011	D1.7			12% arom. ULSD	2xUDDS	3.79	Y	4.57	4.5	0.8	0.2	252	249	443	0.87	0.00
	7/14/2011	D1.10			12% arom. ULSD	2xUDDS	3.30	Y	4.55	3.8	1.2	0.1	287	143	384	0.60	0.00
	7/15/2011	D1.11			9% arom. ULSD	2xUDDS	3.11	Y	4.55	4.1	1.5	0.2	280	186	440	0.67	0.00
	7/19/2011	D1.14			9% arom. ULSD	2xUDDS	3.12	Y	4.51	4.8	0.9	0.2	247	140	373	0.60	0.00
	7/20/2011	D1.15			9% arom. ULSD	Forced Regen	3.10	Ν	n/a	6.0	1.9	4.4	243	299	335	0.73	2.13
	6/9/2011	D2.2		^a DOC, DPF	EPA hybrid ULSD	2xUDDS	3.14	Ν	4.92	0.3	0.0	1.1	107	0.4	0	0.13	0.00
	6/16/2011	D2.13			12% arom. ULSD	2xUDDS	3.28	Y	4.93	n/a	n/a	0.3	248	250	727	1.10	0.00
	6/10/2011	D2.3			28% arom. ULSD	2xUDDS	2.98	Y	4.93	1.4	0.0	1.0	284	650	842	1.73	0.00
	6/13/2011	D2.8	2007		28% arom. ULSD	2xUDDS	3.40	Y	4.81	2.7	1.0	-0.3	143	99	201	0.53	0.00
	6/14/2011	D2.7			12% arom. ULSD	2xUDDS	3.14	Y	4.97	2.8	1.3	-0.1	224	142	599	0.80	0.00
	6/15/2011	D2.12			12% arom. ULSD	2xUDDS	3.13	Y	4.91	1.0	0.5	0.2	303	180	727	0.93	0.00
	6/17/2011	D2.18			12% arom. ULSD	Forced Regen	3.12	Y	n/a	11.6	7.5	3.2	240	468	360	0.93	24.87
	6/22/2011	D3.1			12% arom. ULSD	2xUDDS	3.45	Y	5.02	56.2	38.2	80.8	301	1057	436	1.73	244.69
	6/23/2011	D3.4			12% arom. ULSD	2xUDDS	3.00	Ν	5.02	43.6	6.7	86.6	235	860	475	1.20	330.12
↓	6/24/2011	D3.5	2006	^a none	12% arom. ULSD	3xcreep+idle	3.26	Ν	0.86	4.1	1.3	7.2	48	551	409	0.93	257.02
	6/28/2011	D3.9			28% arom. ULSD	2xUDDS	2.91	N	4.95	50.0	8.3	94.1	272	1059	434	1.33	319.49
	6/29/2011	D3.10			28% arom. ULSD	2xUDDS	3.01	Ν	4.95	45.1	7.6	91.7	275	1074	195	1.73	318.78
	6/30/2011	D3.13			9% arom. ULSD	2xUDDS	3.15	N	5.14	38.6	6.8	87.8	256	933	485	1.47	285.20
	7/1/2011	D3.14			9% arom. ULSD	2xUDDS	2.99	N	5.13	34.1	6.5	93.8	261	932	445	1.33	271.46
	6/11/10	D/I 1				Cold LIC	4.10	N	11.0	C1 4	2.0	97.0	101 0	840	00	1 20	109.27
Т	6/14/10	D4.1	2005	DOC			4.10	N N	11.9	71.4	3.0	87.9	181.2	840	90	1.30	198.37
Ы	6/19/10	D5 2					1.16	N	11.7	71.4	8.4	130.2	228.8	1326	154	0.50	124.42
đ	6/17/10	05.3	2001	none	B100		3.20	N	14.4	61.8	14.4	94.9	147.1	1570	0	2.20	81.77
	6/16/10	D5.2	2001	none	B100		3.78	N	13.0	26.1	9.3	33.3	180.8	1570	0	3.00	54.95
V	0/10/10	05.1			B100		0.68	Ň	13.7	18.7	7.4	34.0	165.9	15/0	0	0.50	50.16
Bink	7/18/2011	dyn blank	n/a	n/a	n/a	n/a	3.21	Y	n/a	4.5	0.5	0.6	1	397	274	0.73	0.00



Figure 3.6. Experimental design matrix of all tested combinations of vehicles (D1 through D5) with different aftertreatment systems (no AT, DOC, DOC+DPF, DOC+DPF+SCR), driving cycles (UC, UDDS, creep, regen) and fuels (D=commercial ULSD, BD=100% biodiesel and L=low-, M=medium-, and H=high-aromatic ULSD). Duplicate experiments are not shown.



Figure 3.7. The speed vs. time profiles of the three different driving cycles used in the smog chamber experiments.



Figure 3.8. Test set-up used for characterizing the photo-oxidized motor vehicle emissions (not to scale).

3.7.1 Wall Loss Rate Correction for Nucleation

Particle loss to chamber walls is a size-dependent process (smaller particles are lost faster); therefore, in regeneration experiments where a major fraction of the particle mass is created during a nucleation event, we must modify the wall loss rate to account for the more rapid loss of nucleation mode particles compared to BC (which is in the accumulation mode). In these cases a large fraction of the OA mass is not internally mixed with BC. We corrected the wall loss rate, k, in these experiments by assuming that wall loss of nucleation mode particles is governed by Brownian diffusion. Crump and Seinfeld derived an expression for the size-dependent wall loss rate for particles in a spherical chamber of radius R

$$k_w(D_p) = \frac{6\sqrt{k_e D}}{\pi R} D_1 \left(\frac{\pi v_s}{2\sqrt{k_e D}}\right) + \frac{v_s}{4R/3}$$
(10)

where *D* is the Brownian diffusivity for particles of diameter D_p , k_e (units of time⁻¹) is a function of the turbulent kinetic energy in the chamber, v_s is the gravitational settling velocity of the particle (negligible for nucleation mode particles) and $D_1(...)$ is the Debye function [80].

Equation (10) indicates that the wall loss rate scales with the square root of diffusivity, which in turn, is inversely proportional to particle diameter [39]. We therefore scale the wall loss rate of the nucleation mode, k_{nuc} , using the wall loss rate of the primary mode, k, and the diameters of the nucleation mode, d_{nuc} , and the primary mode, d

$$k_{nuc} = k \cdot \sqrt{\frac{d}{d_{nuc}}} \tag{11}$$

3.7.2 AMS Corrections: Comparison with SMPS Measurements

Theoretically, the sum of the PM mass from the non-refractory components (measured by the AMS) and BC (measured by the aethalometer) should be equal to the mass calculated from the SMPS size distributions. These three sets of data provide two independent methods of calculating PM, but each method has limitations, complicating the comparison.

First, the SMPS measures particle mobility diameter, while the AMS measures mass. To convert SMPS measurements to mass one must assume a particle shape and density. We assume that particles are spherical with average density of 1 g/cm³. However, fractal-like particles will cause the SMPS to overestimate the spherical equivalent diameter and therefore overestimate particle mass. While commonly made, the unit density [81] and sphericity [82, 83] assumptions have both been shown to not always be valid for aerosol with high EC (e.g., diesel emissions). After SOA production begins the sphericity assumption improves as the organics coat the primary particles, making them more spherical [60].

Second, the mass measured by the AMS will be less than the true PM mass due to three artifacts whose product is referred to as the AMS collection efficiency, C_e :

$$C_e(d_{va}) = E_L(d_{va}) \times E_S(d_{va}) \times E_B(d_{va})$$
(12)

where d_{va} is the particle vacuum aerodynamic diameter. The transmission efficiency, E_L , of the AMS's aerodynamic lens is size-dependent with a detection window that falls off above 600 nm and below 120 nm [84]. E_S is the striking efficiency, which refers to the tendency of non-spherical particles to miss the AMS's vaporizer as they are conveyed from the time-of-flight chamber. E_B quantifies the fraction of particles that bounce off of the AMS's vaporizer before they are measured. Bounce is a function of particle phase (solid/liquid), particle acidity and

ambient RH, among other factors. For an internally mixed aerosol (which is likely in these experiments once SOA forms), the same collection efficiency should be used for all chemical species [85]. Losses due to striking efficiency appear to be less than 20% for ambient particles [86].

In several of the MDDV experiments the sum of the non-refractory components and BC were significantly lower than the mass calculated from the SMPS size distributions (assuming spherical particles and density of 1 g cm⁻³). Such deviations are likely due differences in collection efficiency (e.g., E_S and E_B), and we assume that the difference in mass has the same chemical composition as the speciated components. We then calculate a scaling factor, $AMS_{s.f.}$, that increases the sizes of the four colored wedges in Figure 3.9 proportionally such that their sum closes the gap with the SMPS measurement (dashed line). The scaling factor is

$$AMS_{s.f.} = \frac{C_{SMPS} - C_{BC}}{C_{org} + C_{SO_4} + C_{NO_3} + C_{NH_4}}$$
(13)

where C_{SMPS} is the total particle concentration measured by the SMPS, C_{BC} is the black carbon concentration measured by the aethalometer, C_{org} , C_{SO_4} , C_{NO_3} , and C_{NH_4} are the concentrations of organics, sulfate, nitrate and ammonium measured by the AMS. The values for $AMS_{s.f.}$ were calculated for each time step after nucleation, excluding the times when the aerosol passed through the thermodenuder and then used to scale the AMS data for the MDDV. We set a maximum value of 2.0 for the $AMS_{s.f.}$.



Figure 3.9. Comparison of the sum of BC (measured by the aethalometer), organics, sulfate, nitrate and ammonium (measured by the AMS) against the total particle mass measured by the SMPS. Data are not wall loss corrected.

Table 3.5. Dynamometer driving test cycles. The UC was used with the MDDV, and the 2xUDDS and 3xcreep+idle were used with the HDDV. The older FTP-75 cycle was not used in these tests, but we include it for reference since it was more commonly used in the past.

driving cycle	duration (s)	distance (mi)	avg speed (mph)	max speed (mph)	max accel (mph/s)	stops/ mile	% idle	notes
UC	2035	9.8	24.6	67.0	6.2	1.52	16.4	600 s hot soak w/o emissions sampling is not included in avg speed or % idle values
2xUDDS	2125	11.1	18.8	58.0	4.4	2.52	33.4	UDDS cycle is run 2 times consecutively
3xcreep + idle	2553	0.377	1.8	8.2	2.3	24.17	42.3	creep phase of the 4-phase HHDDT (251 s each) run 3 times + 1800 s idle (not included in avg speed or % idle values)
FTP-75	1377	7.5	19.6	56.7	3.3	2.41	19	for comparison only; not used in this study

Sources: http://www.dieselnet.com/standards/cycles/hhddt.php http://www.arb.ca.gov/msei/onroad/briefs/Publication3.pdf



Figure 3.10. Aromaticity of the three fuels used in the HDDV experiments is positively correlated with the aromaticity of their combustion emissions. Two duplicate experiments with each fuel are shown; in all six experiments driving cycle is 2xUDDS and vehicle is D3.



Figure 3.11. The weight percent of 14 different classes of compounds in the (a) low-aromatic, (b) mid-aromatic and (c) high aromatic content fuels used in the heavy-duty diesel vehicle experiments as a function of carbon number.
	SOA precursor	SOA Vield Cases	OH rxn rate (cm ³ -
Hydrocarbons	text)?	(Fig. 4, main text)	molec ⁻¹ sec ⁻¹)
ethane	no	4	2.48E-13
ethene	no	4	8.52E-12
propane	no	4	1.09E-12
propene	no	4	2.63E-11
methylpropane	no	4	2.12E-12
ethyne	no	4	8.15E-13
n-butane	no	4	2.36E-12
1,2-propadiene	no	4	9.82E-12
trans-2-butene	no	4	6.40E-11
1-butene	no	4	3.14E-11
2-methylpropene	no	4	8.69E-11
cis-2-butene	no	4	5.64E-11
2,2-dimethylpropane	no	4	6.69E-13
2-methylbutane	no	4	3.60E-12
1,3-butadiene	no	4	6.66E-11
1-propyne	no	4	7.14E-12
1,2-butadiene	no	4	2.60E-11
trans-2-pentene	no	4	6.70E-11
3-methyl-1-butene	no	4	5.14E-11
1-pentene	no	4	3.14E-11
2-methyl-1-butene	no	4	6.10E-11
cis-2-pentene	no	4	6.50E-11
1-buten-3-yne	no	4	4.01E-11
2-butyne	no	4	2.73E-11
1-butyne	no	4	8.10E-12
benzene	yes	1, 2, 3, 4	1.22E-12
toluene	yes	1, 2, 3, 4	5.63E-12
octane	yes	1, 2, 3, 4	8.11E-12
ethylbenzene	yes	1, 2, 3, 4	7.00E-12
m-/p-xylene	yes	1, 2, 3, 4	1.70E-11
styrene	yes	1, 2, 3, 4	5.80E-11
o-xylene	yes	1, 2, 3, 4	1.36E-11
nonane	yes	1, 2, 3, 4	9.70E-12
decane	yes	1, 2, 3, 4	1.10E-11
undecane	yes	1, 2, 3, 4	1.25E-11
dodecane	yes	1, 2, 3, 4	1.32E-11
Carbonyls			
formaldehyde	no	4	9.37E-12
acetaldehyde	no	4	1.50E-11
acrolein	no	4	2.58E-11
acetone	no	4	1.70E-13
propionaldehyde	no	4	2.20E-11
crotonaldehyde	no	4	3.62E-11
methacrolein	no	4	2.90E-11
MEK	no	4	1.33E-12
butyraldehyde	no	4	2.40E-11
benzaldehyde	yes	1, 2, 3, 4	1.20E-11
valeraldehyde	no	4	2.74E-11
m-tolualdehyde	yes	1, 2, 3, 4	1.70E-11
hexanal	no	4	3.00E-11
Other			
unidentified Kovats < 800	no	4	2.79E-11
unidentified Kovats ≥ 800	Ves	1, 2, 3, 4	1.67F-11
unspeciated NMOG	no	3.4	1.00E-11
SVOC/IVOC	Ves	2, 3, 4	3.00F-11
,	,	_, 3, 1	

Table 3.6. Categories of NMOGs as discussed in Figures 3 and 4 of main text.

Chapter 4: Off-road Engines: Characterizing Primary Emissions and Secondary PM Production

4.1 Introduction

Unregulated in the US until 1995, the combustion emissions from both small (< 19 kW) off-road engines (SORE) used in lawn and garden applications (e.g., lawnmowers, leaf blowers, trimmers) as well as transportation refrigeration units (TRU) used to cool perishable cargo during transport have come under increasing regulatory scrutiny in recent years as their impact on air quality has become clearer. While responsible for only about 2% of the fuel consumption of on-road vehicles, some SORE—which include both 2-stroke configurations, typically used to power handheld equipment and 4-stroke configurations for non-handheld applications—are known to have high emissions of gas- and particle-phase pollutants [1].

It has been estimated that SORE used in lawn and garden equipment emit 6 million tons of pollutants annually (in 2007), accounting for 5–10% of *total* US emissions of carbon monoxide (CO, nitrogen oxides (NOx), hydrocarbons (HC), and fine particulate matter (PM2.5) [2, 3]. Another study estimates that there were 5×10^8 4-stroke SORE in operation globally (in 2007) producing over 10^6 metric tons of HC+NOx and 5×10^7 metric tons of CO₂; this estimate would be significantly higher if the 2-stroke contribution were added since they constitute ~30% of SORE annual sales globally [4]. TRU are generally powered by larger diesel engines (ranging between 5 and 27 kW with a mode of ~26kW), and older models without emission control devices likely emit high levels of PM. Although there are a large number of TRUs in the U.S.— a 2011 report by the California Air Resources Board estimates 176,000 TRU (including out of state TRUs) operating within CA—we are not aware of any peer-reviewed studies of their emissions.

While the primary PM emissions from some TRU and SORE are known to be high, it is not yet known how much they contribute to the large amount of secondary particulate matter that has been observed in the atmosphere. Secondary PM forms when gaseous precursors emitted from "the tailpipe" oxidize in the atmosphere, become less volatile and partition into a condensed phase. When the precursor gases are organic, the secondary PM is referred to as secondary organic aerosol (SOA). Laboratory studies of many other combustion sources, including light duty gasoline vehicles, medium- and heavy-duty diesel vehicles, biomass burning and jet aircraft [5-10] have demonstrated that the mass of SOA often exceeds the mass of the primary PM (the organic fraction is primary organic aerosol, POA) emitted by these sources. Furthermore, numerous ambient studies have shown that SOA dominates POA even in urban areas with substantial POA emissions [11-13]. Thus, although organic aerosol, particularly SOA, is a major component of atmospheric PM, its sources remain inadequately characterized [14, 15].

Given their high primary PM emissions, it is reasonable to hypothesize that SORE emissions also contribute substantially to SOA production. However, aside from several studies of SOA production from the emissions of a small diesel generator [16, 17], we are unaware of any published reports of SOA production from smaller engines or TRU. Hung and Wang [18] characterized emissions from a small (124 cc engine displacement) motorcycle and reported that "diluted motorcycle exhaust has a high potential to form...SOA under UV irradiation," but they do not quantify this potential.

This study investigates primary gas and particle emissions and SOA formation from six SORE and one TRU. The engines include both diesel and gasoline models, 2- and 4-stroke configurations and a range of sizes (displacements). They were operated over certification cycles. The primary emissions of all engines were characterized, and dilute emissions from two of them were injected into a smog chamber and then photo-oxidized to characterize secondary PM formation.

4.2 Materials and Methods

Sixteen SORE/TRU experiments were conducted at the California Air Resources Board's (CARB) Haagen-Smit Laboratory (HSL), in El Monte, California and at Carnegie Mellon University (CMU). These experiments consisted of (a) nine primary tests at HSL in which only primary PM and gas emissions were characterized, (b) three chamber tests at HSL in which secondary organic aerosol formation and gas-phase species were measured in the smog chamber (primary PM and gas-phase data in the constant volume sampling system (CVS) were also collected for these experiments) and (c) four chamber experiments at CMU with the same two SOREs tested in the chamber experiments at HSL. For one of the three chamber tests at HSL, instrument problems prevented us from obtaining speciated PM data, but measurements of primary and gas-phase data in the CVS as well as total particle concentration, black carbon (BC) and organic gases in the chamber were acquired. Subsequent sections of this report describe the engines, fuel, test cycles and experimental set-up for each of these three categories of tests. A

schematic of the combined suite of instruments used in primary and chamber tests is provided in Figure 3.8 of the SI.

4.2.1 Engines

Six gasoline SORE from a variety of applications (backpack leaf blower, soil tiller, string lawn trimmer and lawnmower) and a larger diesel engine for a transportation refrigeration unit (TRU) were tested; engine details are provided in Table 4.1. The SORE included both 2- and 4- stroke engines manufactured between 2002 and 2006; however, most of these had seen little or no use, as they were purchased by CARB for test purposes only. The TRU engine was older (1998) and had been in service for > 1000 hours. The CARB executive orders for each of these seven engines indicate that no catalyst or other aftertreatment was required to meet the governing emission standard (Title 13, California Code of Regulations, (13 CCR) Section 2403(b)). While the test engines were not chosen with the specific goal of representing the existing fleet of SORE and TRU, data from them provide a reasonable first estimate of the range of primary emissions and SOA formation that can be expected from these ubiquitous sources.

Table 4.1. Specifications of engines used in both smog chamber and primary experiments. The experiment naming convention is based on the engine ID. The complete experimental design matrix is provided in the SI.

engine ID	chamber /primary	model year	application	eng. size (cc)	max HP	engine type	test cycle	HC+NOx standard (g/kWh)	CO cert. level (g/kWh)	PM cert. level (g/kWh)	est. op. time (h)
SORE2S-1	С	2002	blower	49	2.95	2-stroke gas	2-mode Cycle C	50	536	2.0	<100
SORE4S-4	С	2004	blower	65	4.0	4-stroke gas	2-mode Cycle C	54	400	n/a	0
TRU4S-1	Р	1998	TRU	2200	34.8	4-stroke diesel	4-mode EPA TRU Cycle	pre-std	pre-std	pre-std	1000+
SORE4S-1	Р	2004	soil tiller	205	8.5	4-stroke gas	6-mode Cycle A	12	410	n/a	8+break in
SORE2S-2	Р	2005	trimmer	25	1.3	2-stroke gas	2-mode Cycle C	50	536	2.0	0
SORE4S-2	Р	2005	trimmer	31	1.2	4-stroke gas	2-mode Cycle C	50	536	2.0	0
SORE4S-3	Р	2006	lawnmower	160	5.5	4-stroke gas	6-mode Cycle A	16.1	549	n/a	26+break in

4.2.2 Fuels

The same California commercial summertime gasoline was used in all the SORE tests

(both primary and secondary), and a summary of some of its important characteristics is

provided in Table 4.2; further detail is provided in Table 4.5 of the SI. Both of the TRU

experiments were run with the same CA ultralow sulfur diesel fuel, but no detailed

compositional analysis was available for this fuel.

Table 4.2. Fuel analysis of gasoline used in all spark-ignition engine SORE experiments. The method of analysis and the relevant ASTM are also provided. Further compositional analysis and an elemental mass balance are provided in Table 4.5 of the SI.

MTBE (wt%)	oxygen (mass%)	benzene (vol%)	aromatics (vol%)	olefins (vol%)	olefins/ naphthalenes (mass%)	poly- naphthalenes (mass%)	RVP (psi)	T ₁₀ (°F)	T ₅₀ (°F)	T ₉₀ (°F)	sulfur (ppm)	density (g/ml)
ASTN GC	/I 4815, C/FID	ASTM GC	D5580, :/FID	ASTM 6550 SFC			ASTM D5191		ASTM D8	6	ASTM 5453 ANTEK	ASTM D4052
6.08	2.11	0.56	23.8	5.20	12.38	0.08	6.8	135	212	313	8.80	0.7410

4.2.3 Test Cycles

4.2.3.1 Engine Dynamometer Test Cycles Used in Primary Experiments

SORE compliance testing in the U.S. and Europe is based on the J1088 test procedures in which several different steady-state test cycles are described for handheld and non handheld products. Each engine in this study was tested using the same cycle as prescribed in CARB's certification testing procedure (see Table 4.1). The SORE were operated for 20 minutes at 50% throttle to bring the engines to a steady-state prior to each test cycle. In order to simulate actual operation, the test cycles have between two and six separate phases or modes during which the engine is operated at a specified power level. Each mode is weighted according to its relative importance during the product's expected usage. Cycle A and B (non handheld products) have

intermediate load test points, whereas Cycle C (handheld products) has full throttle and idle

modes only. The EPA TRU steady-state cycle consists of four equally weighted modes. Three

different dynamometers—a 5 hp, 30 hp and 50 hp—all from DyneSystems, were used to load the

SOREs and TRU during the primary tests at HSL.

Table 4.3. Specifications for the (a) 6-mode Cycle A used in the 4-stroke SORE primary tests, (b) EPA TRU test cycle and (c) 2-mode Cycle C tests used for chamber experiments and 2-stroke SORE primary tests. Adapted from [4, 19].

(a)	mode	1	2	3	4	5	6
()	weight	0.09	0.20	0.29	0.30	.07	.05
	rated speed	85%	85%	85%	85%	85%	idle
	torque	100%	75%	50%	25%	10%	0%
<i>(</i> 1)							
(b)	mode	1	2	3	4		
()	weight	0.25	0.25	0.25	0.25		
	rated speed	100%	100%	65%	65%		
	torque	75%	50%	75%	50%		
(C)	mode	1	2				
()	weight	0.85	0.15				
	rated speed	100%	idle				
	torque	100%	0%				

4.2.3.2 Smog Chamber Test Cycles

Unlike the primary experiments, the two engines used in the chamber experiments were not operated with an engine dynamometer. Instead they were installed in leaf blowers, which provided the load. The SORE were warmed up for 20 minutes at 50% throttle to bring the engines to a steady-state operating temperature before beginning the test cycle. These engines were used to power two different leaf blowers, and they were loaded as prescribed by the 2-mode C test cycle by adjusting the blowers' throttles to 100% power for 85% of the test period (24 minutes total) and idle for 15% of the time. Emissions were added to the chamber over the entire C test cycle; thus, these experiments represent cycle average emissions. The test cycle for the CMU chamber experiments was similar to the C test except that without the additional dilution provided by the CVS at HSL it was necessary to reduce the total test cycle to 2.5 minutes to limit the amount of PM injected into the chamber to approximately the same (atmospherically relevant) levels as at HSL. Although the overall cycle was shorter with the CMU tests, the ratio of full power operation to idle operation was maintained at 85/15 as with the experiments at HSL.

4.2.4 Experimental Setup and Analytical Equipment

4.2.4.1 Primary Experiments at HSL

Figure 3.8 shows a schematic of the experimental set up. Emissions were sampled using a Constant Volume Sampler (CVS) nominally following the procedures outlined in the Code of Federal Regulations Part 1065. Briefly, the entire raw exhaust is diluted (not less than 1:6) with HEPA-filtered air in the CVS (Horiba-7200 SLE). The CVS was operated at a combined (dilution air plus exhaust) flow rate of between ~350 ft³/min and 1000 ft³/min, depending on the expected emission level of the engine.

ARB characterized both standard and speciated emissions of gaseous and PM pollutants. Standard operating procedures for the ARB methods are available online (http://www.arb.ca.gov/testmeth/slb/exhaust.htm). Measured gaseous emissions included carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), nitric oxide (NO), nitrogen oxides (NO_x), and non-methane organic gases (NMOG). Gaseous emissions from dilute exhaust in the CVS were sampled and stored in baked Tedlar® bags (up to 80 L). The system collects samples of both filtered dilution air (immediately downstream from the CVS HEPA filters) and diluted exhaust (by phase) from which emissions are determined. Exhaust gas analysis is performed with an AVL-AMA 4000 system. Non-methane organic gases are measured using Flame Ionization Detection (FID), methane (CH₄) by FID-gas chromatography, oxides of nitrogen (NO_x) by chemiluminescence (CLD 4000), and carbon monoxide (CO) and carbon dioxide (CO₂) by non-dispersive Infrared (NDIR) detectors (IRD-4000).



Figure 4.1. Test set-up used to characterize SORE and TRU emissions (not to scale). Primary PM and gas-phase compounds in the constant volume sampling line were analyzed (data output shown in boxes denoted with the * symbol). For a subset of the experiments conducted at HSL, a portion of the dilute emissions from the CVS were also photo-oxidized in the smog chamber, and the secondary PM production and gas-phase compounds were characterized by a suite of instruments sampling through an unheated transfer line from the chamber (shown at the upper right of the figure).

Concentrations of speciated C_2 to C_{12} hydrocarbons in the diluted exhaust were

determined from the samples collected in Tedlar® bags following standard operating procedure

MLD 102 / 103 Version 2.2 (http://www.arb.ca.gov/testmeth/slb/sop102-103v2-2.pdf). Briefly, the analytical procedure uses two gas chromatographs (GCs): one for analyzing the light-end (C_2 to C_5) hydrocarbons and the second for analyzing the mid-range (C_6 to C_{12}) hydrocarbons, equipped with cryogenic pre-concentration (cryotrap) and automated, gas-phase sampling valve systems. The light-end GC uses a Varian Al₂O₃/KCl porous layer open tubular (PLOT) analytical column [50 m x 0.32 mm inner diameter (ID)] to separate the hydrocarbon mixture. The mid-range GC uses a Varian DB-1TM analytical column (60 m x 0.32 mm ID, 1 um film thickness) for separate. FIDs are used for hydrocarbon detection and quantification. The FIDs are calibrated with NIST-traceable propane standards. System performance is routinely evaluated using a quality control standard that contains a suite of hydrocarbons.

Dilute exhaust samples for carbonyl analysis are collected from the CVS using a Horiba Micro II Impinger with DNPH supplied by SEP-PAK[™] (silica cartridges, Plus Short Body 360 mg). The 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges were analyzed using standard operating procedure MLD 104 Version 3.0

(http://www.arb.ca.gov/testmeth/slb/sop104v3.pdf). The cartridges were extracted with 5.0 milliliters (mL) acetonitrile and analyzed using a high-performance liquid chromatograph (HPLC) with an ultraviolet (UV/VIS) detector to quantify carbonyls.

PM sampling from the CVS is done using an AVL AMA 4000 Advanced sampling system compliant with the 2007 CFR-1065 regulations. ARB operated three separate filter trains: Train #1 consisted of a Teflon® filter (47mm, Pall-Gelman, Teflo R2PJ047); Train #2 consisted of two quartz filters (47 mm, Pall-Gelman, Tissuquartz 2500 QAOUP) in series; and Train #3 consisted of a Teflon® filter followed by a quartz filter. Following the procedures of CFR-1065, all of these filter trains were maintained at 47°C. The flow rate through each train was 44.7 L/min.

The Teflon® filter in Train #1 was analyzed gravimetrically to determine PM mass emissions following standard operating procedure MLD145 (http://www.arb.ca.gov/testmeth/slb/sop145v5_1.pdf). Pre- and post-test filter mass is determined using a microbalance after equilibration at 22°C and 35% relative humidity for 24 hrs. PM mass is defined as the difference between the buoyancy corrected post- and preweights of each Teflon® filter.

After gravimetric analysis, the Teflon® filter in Train #1 was extracted and analyzed by ion chromatography for water soluble anions (chloride, nitrate and sulfate) and cations (sodium, ammonium, potassium, magnesium and calcium) following standard operating procedure MLD 142 (http://www.arb.ca.gov/testmeth/slb/sop142v2-0.pdf). The ions are extracted from the filter by sonication in deionized (DI) water with ~1% isopropyl alcohol. The resulting extracts are stored in a refrigerator in order to settle particles and then analyzed by ion chromatography with a conductivity detector.

All three quartz filter samples were analyzed for organic and elemental carbon (OC and EC) following standard operating procedure MLD 139

(http://www.arb.ca.gov/testmeth/slb/sop139v1-0.pdf). Briefly, punches from each quartz filter were analyzed using a DRI (Desert Research Institute) Thermal/Optical Carbon Analyzer Model 2001using the IMPROVE-A protocol [20]. Prior to sampling, quartz filters were baked at 550°C in air for at least 12 hours to remove any residual carbon.

Low-volatility organics were sampled from dilute exhaust in the CVS using two parallel sample trains of a quartz filter (47 mm, Pall-Gelman, Tissuquartz 2500 QAOUP) followed by

two sorbent tubes (Gerstel 6mm OD/4.5mm ID glass tubes filled with 290mg of a granular porous type of polymer, 2,6-Diphenyl p-phenyleneoxide, called TenaxTM TA) in series. The inlet line and sample box (filter and sorbent tubes) were maintained at 47°C. The flow rate through each quartz filter was 9.9 L/min and the flow rate through the sorbent tubes was 300 mL/min. A bypass line was used to exhaust the excess flow downstream of the quartz filter.

Filter and sorbent tube samples were analyzed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). Prior to sampling, the quartz filters were baked at 550°C in air for at least 12 hours to remove any residual carbon. The Tenax[™] TA sorbent tubes were cleaned and conditioned via thermal desorption at 320°C under a constant 50 mL/min flow of ultrahigh purity helium.

A major objective of this project is to investigate the SOA formation of dilute exhaust from off-road engines. Table 4 lists the different measurements of gas-phase organics, which are grouped into eight different categories. Collectively, five of the eight groups are based on speciated emissions, which included 203 individual compounds (groups 2-6 in Table 3.3). Group 7 included both speciated data and a co-eluting set of compounds referred to as an unidentified complex mixture (UCM), but for this study these two subcategories within group 7 are lumped together. The FID measurement of THC in group 1 is assumed to include all gasphase organics except IVOCs and SVOCs, since the latter are higher molecular weight and partition to the particle phase (where they are not seen by the GC-MS) more readily. Group 8 was defined by subtracting from group 1 all speciated and lumped compounds that were assumed to be measured by the FID (i.e., groups 2-6).

Table 4.4. Eight different classes of organic gas-phase compounds characterized from the CVS. The number/type of compounds is reported as well as the laboratory techniques used to acquire and quantify the gases.

group	species in group	<u># species</u>	sampling method	method of quantification
1	total hydrocarbons		heated Tedlar bags	heated FID
2	methane	1	heated Tedlar bags	heated FID
3	low MW VOCs (speciated)	25	Tedlar bag	GC-MS with a Varian Al_2O_3/KCI PLOT column
4	mid MW VOCs (speciated)	164	Tedlar bag	GC-MS with a Varian DB- 1™ column
5	low MW carbonyls	11	DNPH cartridges	HPLC with a UV detector
6	aromatic carbonyls	2	DNPH cartridges	HPLC with a UV detector
7	S/IVOCs	lumped group	Quartz filter, Tenax tube	TD-GC-MS
8	NMOG balance	lumped group	n/a	$group_1 - \sum_{i=2}^{\circ} group_i$
Total spe	ciated compounds	203		

Concentrations of individual organic compounds in the quartz filter and Tenax[™] TA sorbent samples were determined using multipoint calibration curves developed using authentic standards for a suite of target compounds and a deuterated internal standard to track analyte recovery [21].

4.2.4.2 Smog Chamber Experiments at HSL

In addition to the measurements from the CVS described above, combustion emissions from two SORE were characterized in a smog chamber at HSL. In these experiments emissions from the CVS were transferred via heated (47 °C) Silcosteel (i.e., passivated internal bore) tubing to a 7 m³ Teflon smog chamber where they were photochemically aged [8]. Before each experiment the chamber was cleaned by flushing with HEPA- and activated carbon-filtered air overnight. Emissions were added to the approximately half-filled chamber over the entire C test

cycle (see Smog Chamber Test Cycles). The exhaust was diluted in three stages: first, it was diluted 10:1 with ambient temperature HEPA-filtered air in the CVS; it was then diluted 8:1 with 47°C HEPA- and activated carbon-filtered air using Dekati ejector diluters in the transfer line; finally, it was diluted 2:1 in the smog chamber.

After adding exhaust, nitrous acid (HONO) was bubbled into the chamber as a hydroxyl radical (OH) source, and VOC:NOx ratios were adjusted by adding either propene or NO to the chamber. After ~1 h of primary characterization, the emissions were photo-oxidized by exposing them to UV lights (Model F40BL UVA, General Electric). Seed aerosol was not added in any of the chamber experiments except for the dynamic blank experiment.

An array of instruments was used to characterize gas- and particle-phase pollutants inside the chamber. Particle number distributions were measured with a scanning mobility particle sizer (SMPS, TSI, Inc., classifier model 3080, CPC model 3772). Non-refractory particle mass and chemical composition were measured with a quadrupole Aerosol Mass Spectrometer (AMS, Aerodyne, Inc.). Gas-phase organic species were measured with a proton transfer reaction mass spectrometer (PTR-MS, Ionicon) operated in selected-ion mode with a time resolution of ~2.5 min. The PTR-MS was calibrated daily using a custom gas standard from Spectra Gases. Dedicated gas monitors were used to measure CO₂ (LI-820, Li-Cor Biosciences), SO₂, NOx, CO, and O₃ (API-Teledyne Models 100E, 200A, 300A and 400E); monitors were zeroed daily and calibrated at least weekly. A seven channel aethalometer (Magee Scientific, Model AE-31) measured black carbon (BC), and the aethalometer attenuation measurements were corrected for particle loading effects using the method of Kirchstetter and Novakov [22].

The fragmentation table from Allan et al. [23] was used to interpret AMS data. The contribution of gas-phase CO_2 to the AMS m/z 44 signal was corrected using the measured CO_2

concentrations. The background corrected CO_2 levels in the chamber ranged from 0 to 70 ppm. There was no evidence of organic particle signal at m/z 28 (CO^+). Organic and inorganic nitrates fragment into NO⁺ and NO₂⁺ in the AMS, but organic nitrates generally have a considerably higher ratio of NO⁺ to NO₂⁺, making it possible to apportion nitrate signal between the two classes. Using the approach of Farmer et al. [24], only a minor fraction (typically <5%) of the nitrate mass (which was usually quite small) was attributable to organics.

Turning on the UV lights during the chamber experiments initiated photo-oxidation, and hydroxyl radicals (OH) were produced at that time. The OH levels in the chamber were inferred from the decay of VOCs (e.g., toluene, xylenes, TMB, propene) measured with the PTR-MS [25]. Typical experiment average OH levels were $3-5x10^6$ molecules cm⁻³, which is within the range of summer daytime atmospheric concentrations [26]. OH levels were generally higher during the initial stages of the photo-oxidation phase of the experiment and then fell as the HONO was photolyzed.

A summary of selected initial and final chamber conditions is provided in Table 4.7. Initial POA concentrations inside the chamber ranged from $0.9-4 \ \mu g/m^3$ for the 2-stroke and from 12.1-20 $\ \mu g/m^3$ for the 4-stroke tests; these conditions in the chamber span typical urban conditions. The mixing ratios of individual single-ring aromatics in the chamber were typically less than 20 ppb. Initial NOx concentrations in the chamber were between 0.2 and 1.8 ppm. The smog chamber was located in a large air conditioned space; the temperature and humidity in the chamber varied between 25-28°C and 4-13%.

A blank experiment was run to assess background levels of gases and particles in the chamber. The blank experiment was done by adding CVS air to the chamber (no exhaust), ammonium sulfate seed aerosol and HONO. Problems with the AMS prevented the collection of

speciated aerosol data during the blank experiment, but the SMPS data clearly indicate no increase in PM mass during photo-oxidation of CVS air without vehicle emissions. The BC and net NMOG concentrations in the chamber during the blank experiment were $0.3 \ \mu g \ m^{-3}$ and $0.71 \ ppmC$, respectively. The NMOG concentration includes exogenous propene added to ensure that the experimental procedure in the blank experiment was as similar as possible to that used in the other chamber experiments.

4.2.4.3 Smog Chamber Experiments at CMU

Four chamber experiments were conducted at Carnegie Mellon University to supplement the three CARB chamber experiments. The tests were conducted with the same engines (Table 4.1), using the same fuel and basic test procedures. The tests at CMU did not include a CVS, and fewer species were measured. The goal of these experiments was to increase the robustness of SOA production estimates derived from the chamber experiments at HSL by running duplicate experiments with the same two SOREs. Therefore, experimental protocols for the smog chamber experiments at CMU adhered as closely as possible to those used in the previously described chamber experiments at HSL.

The CMU chamber is similar to the one used at HSL, and detailed descriptions of the CMU chamber facilities have been published previously [17]. The primary differences between these two chambers are that the CMU chamber is slightly larger— $10m^3$ instead of $7m^3$, and it is housed in a temperature-controlled room. The CMU chamber was cleaned by irradiation, heat (40 °C), and continuous flushing with dry, HEPA-filtered and activated carbon-filtered air overnight. After cleaning, the lights were turned off, and the chamber temperature was reduced to 23 °C with an initial relative humidity of ~5%. After warming up the SORE (see Smog

Chamber Test Cycles), combustion emissions were admitted to the chamber through a heated inlet during the test cycle.

Gas-phase data used for calculating OH exposure in the CMU chamber were obtained using a GC-MS (Agilent 6890N gas chromatograph/ 5975B mass spectrometer) instead of the PTR-MS used at HSL. *n*-octane (m/z 57, 17.9 minute retention time) was used as the OH tracer with the GC-MS. Instead of the Q-AMS used in the smog chamber experiments at HSL, the Aerodyne High-Resolution Aerosol Mass Spectrometer was used during the CMU chamber experiments.

4.2.5 Calculation of Emission Factors

Time-based emissions of gas- and particle-phase species measured in the CVS for multimode tests were calculated using the relationship [27]

$$emission_{k} = \sum_{i=1}^{n} E_{i} W_{i}$$
 (14)

where *emission*_k is the time-based emission rate for species k (in g/hr), E is the emission rate in the CVS (in g/hr) for mode i of the test cycle, W is a weighting factor and n is the number of modes in the test cycle. The emissions data are converted to fuel-based emission factors (grams of species per kilogram fuel consumed) from the measured pollutant concentrations using the carbon mass balance approach:

$$EF_{k} = \frac{emission_{k} \cdot x_{c}}{\Delta CO_{2} + \Delta CO + \Delta HC}$$

where *emission*_k is the concentration of species k from Equation (14) in the CVS, x_c is the mass fraction of carbon in the fuel (0.85, see Table 4.5), and ΔCO_2 , ΔCO , and ΔHC are the background-corrected carbon concentration of CO₂, CO and hydrocarbons measured in the CVS (in g-Carbon/hr). In contrast to modern passenger vehicles whose emissions are dominated by CO_2 , the smaller engines tested in this study emitted significant amounts of CO and HC (30-40% of carbon emissions were due to CO and HC); therefore these species cannot be neglected when calculating the fuel-based emission factors.

4.2.6 Quantifying SOA Production

To quantify SOA production in the smog chamber we corrected the measured concentrations of suspended particles to account for losses to the chamber walls. A detailed discussion of these corrections may be found elsewhere [7]; here we provide a brief overview only.

Organic particles and vapors are lost to the chamber walls as a function of time, and total OA is the sum of the measured (via the AMS) suspended mass plus the mass of organics on the chamber walls

$$OA_{total,t} = OA_{sus,t} + OA_{wall,t}$$
(15)

Organics may be lost to the chamber walls as particles or vapors. Loss of organic particles is treated as a first-order process [28] with a rate constant determined from the decay of various non-reactive tracer species (e.g., BC or an inorganic seed)

$$C(t) = C_0 e^{kt}$$

where *C* is the tracer concentration at time *t*, C_o is the initial tracer concentration and *k* is the wall loss rate constant. The wall loss rate constant depends on the size and composition of the particles, turbulence in the chamber, the size and shape of the chamber, and particle charge [29]. Therefore, it was determined for each experiment by fitting each time series of tracer data. The particle wall loss rate ranged from -0.247 to -0.548 hr⁻¹. The loss of condensable organic vapors to wall-bound particles is constrained by considering two limiting cases: the first (Method #1) assumes that no organic vapors condense to wall-bound particles, and the second (Method #2) assumes that organic vapors remain in equilibrium with both wall-bound and suspended particles.

Method #1 provides a lower bound estimate of the SOA mass production; it is equivalent to the " $\omega = 0$ " correction utilized in previous studies [9, 17]. Method #1 assumes that mass transfer resistance to the walls is much greater than to the suspended particles. Assuming no loss of vapors to the walls in Method #1, the rate at which OA mass is lost to the chamber walls is

$$\frac{d}{dt}(OA_{wall}) = OA_{sus}(-k) \tag{16}$$

where OA_{sus} is the AMS-measured (i.e., suspended) OA mass at time *t* and *k* is the negative wall loss rate constant [17]. The total OA in the chamber is calculated by numerically integrating equation (3) and adding the calculated OA lost to the wall to the measured OA concentration (equation (2)).

Method #2 assumes that particles lost to the walls during an experiment remain in equilibrium with the vapor phase. This case corresponds to the " $\omega = 1$ " correction [17]. The total OA mass at time *t* is equal to the suspended particle mass scaled by the ratio of the initial tracer concentration to the exponential fit to the tracer concentration at time *t*

$$OA_{total,t} = \frac{OA_{sus,t}}{e^{kt}} \tag{17}$$

where k is the negative wall loss rate constant of the tracer. As only *suspended* OA is referenced in equation (7), the PM on the wall and in suspension have the same composition.

The loss of organic vapors directly to the chamber walls (in distinction to their loss to wall-bound particles) is highly uncertain, and in keeping with virtually every other chamber study in the literature, we do not account for it here. If it were included, it would *increase* our estimate of SOA production.

Chamber blank experiments performed after filling the chamber with CVS dilution air, HONO, and ammonium sulfate seed particles produced 1-3 μ g/m³ of SOA over a 3 hour photooxidation period. This SOA is likely formed from the residual vapors that desorb from the CVS, transfer line and chamber wall. Therefore, for every chamber experiment we assume an SOA blank of 0 μ g/m³ at t=0 that increases linearly to 2 μ g/m³ of SOA at t=3 h and subtract this artifact from the reported SOA production.

4.2.7 Repeatability

Duplicate primary experiments were performed with five of the seven SORE/TRU test engines. The variability in species measured in the CVS for these duplicate experiments was generally small. For example, the maximum differences between pairs of THC measurements and pairs of CO measurements in the five sets of duplicate experiments were 6% and 11%, respectively.

Although the gas- and particle-phase emissions agreed closely in duplicate chamber experiments (SORE2S-1.1 and SORE2S-1.2 experiments), SOA production during these same two experiments diverged significantly. SOA production for the duplicate experiments conducted at CMU was also significantly different. Lack of repeatability appears to be due to the facts that SOA production is sensitive to VOC/NOx ratio [7, 30-32] and that this ratio was not closely controlled (note the differences in VOC/NOx among the duplicate experiments in Table 4.7). While the experimental variability inherent in performing chamber experiments at two different laboratories (HSL and CMU) and with two different (although similar) chambers cannot be dismissed, this does not appear to be a major factor influencing repeatability. Thus, rather than indicating some uncharacterized bias or large random error (which could undermine conclusions in a study such as this with relatively few repeated experiments), these differences in SOA production in "duplicate" experiments are reasonably predictable, given the differences in VOC/NOx. Indeed, for experiments in which VOC/NOx ratios were better controlled, extensive tests characterizing SOA production from a variety of sources have demonstrated excellent repeatability in each chamber independently [6, 7, 9, 33, 34].

4.3 Results

4.3.1 Primary Emissions

Gas-phase (CO, CO₂, NOx and non-methane organic gases) emission factors (g-pollutant per kg-fuel) for all the experiments performed at HSL with the three classes of engines (SORE 2-stroke, SORE 4-stroke and TRU 4-stroke) are summarized in Figure 4.2a-d with data from repeat experiments averaged before plotting. (The data for the primary SORE and TRU results on which the figure is based are in Table 4.6 of the SI.)

Comparisons between the different engines are complicated by the fact that they were tested using different duty cycles. All of the 2-strokes were tested using the 2-mode Cycle C, but half of the 4-strokes were tested using Cycle C and half were tested using Cycle A, and the TRU is certified according to yet another cycle. However, the test cycles we employed are the ones that were used for engine certification. For example, regulations require that leaf blowers of a certain displacement be tested using Cycle C, regardless of whether they are powered by 2- or 4stroke engines. The test cycles were designed to reflect the type of operation that these devices are expected to see in the field; thus, we expect our data to be a reasonable predictor for realworld operation.

Also shown in these figures are data from a SORE 2-stroke study by Volckens et al. [35], and vehicle emission studies by Gordon et al. [6, 7] for comparison. Volckens et al. tested 23 different 2-stroke engines; here we have selected only the data from the three engines (also non-catalyst engines) they tested that were closest in displacement and year of manufacture to the two different 2-stroke engines that we tested. The data from Gordon et al. are from 64 unique light-duty gasoline vehicles (passenger cars/trucks) binned according to age/emission standard: pre-LEV (MY1987-1993), LEV-1 (MY1994-2003) and LEV-2 (MY2004-2012) [6]. The diesel vehicle data are from tests with two medium duty diesel trucks and 3 heavy-duty diesel trucks with a range of aftertreatment devices [7].

A number of important observations can be drawn from Figure 4.2. First, Figure 4.2a indicates nearly 4-orders of magnitude difference between the very high CO emissions (per mass of fuel) from 2-stroke engines and from the newer (MY2007+) diesel particulate filter (DPF) equipped heavy-duty diesel vehicles ("HDDV+DPF" in the figure). While slightly lower, CO emissions from 4-stroke engines are comparable with 2-strokes. The agreement between our 2-stroke CO measurements and those from Volckens et al. [35] is excellent, given that these two studies tested similar, but not identical, identical 2-stroke engines. Light duty vehicles (LDV) show a clear decreasing trend in CO emissions, with the cleanest LDV (LEV-2) emitting roughly 60 times less CO as 2-strokes and comparable to CO emissions from medium-duty diesel trucks, uncontrolled heavy duty diesel vehicles (HDDV) and the diesel-powered TRU. In agreement

with previous studies, CO emissions from diesels are significantly lower than from gasoline engines [36].

Figure 4.2b indicates that the amount of CO_2 emitted across all vehicle and TRU engines is almost identical—differing by <5%. This is not surprising because these engines have been designed to extract as much energy from the fuel as possible. The designs of 2-stroke and (to a lesser degree) 4-stroke SOREs, on the other hand, are driven by portability and low-cost. Twostrokes tend to emit more unburned and partially burned fuel, as described below. Therefore, we found (in good agreement with Volckens et al.) that CO_2 emissions from 2-strokes and 4-strokes were about 50% and 25% lower than from the vehicles and TRU.

NOx emissions from 2-stroke SOREs are quite low, as corroborated by the data from Volckens et al., and roughly comparable to LDV. Presumably, this is because these engines typically run fuel rich. Four-stroke SORE NOx emissions are an order of magnitude higher than 2-stroke emissions. The introduction of selective catalytic reduction (SCR) systems in many newer HDDV+DPF (especially MY2010+) has reduced NOx emissions by an order of magnitude. The median NOx value for HDDV+DPF plotted in Figure 4.2d includes one truck with SCR and one without. In comparison to the SCR-equipped HDDV, the TRU emits much more NOx; the TRU emits roughly the same NOx (per mass of fuel consumed) as the HDDV without SCR.

Non-methane organic gas (NMOG) emissions contribute to ozone and SOA formation. The NMOG emissions from 2-stroke engines (Figure 4.2d) are almost three orders of magnitude higher than the emissions from the newest LDV (LEV-2). A large fraction of these emissions is likely vaporized, unburned fuel which mixes with post-combustion products as they are being exhausted from the engine cylinder [35]. Our measurements of 2-stroke NMOG are in close agreement with those reported by Volckens et al. While 4-stroke SOREs emit an order of magnitude less NMOG than 2-strokes, their emissions are still very high—approximately three times higher than the median value for the oldest LDV (but probably well below many so-called super-emitters currently on the road). In contrast to the very high NMOG emissions from SOREs, HDDV+DPF emit essentially no measureable NMOG; their values are below the scale of Figure 4.2d. Other studies have also shown that NMOG from diesels is significantly lower than from gasoline engines [36]. NMOG emissions from the TRU are roughly a factor of 2 higher than the uncontrolled HDDV.

The bottom four subplots of Figure 4.2 present the particle-phase data. The total primary PM as well as its organic carbon (OC) and elemental carbon (EC) constituents are summarized in Figure 4.2e-h for the emissions from the seven engines and for the different vehicle categories. (The raw data are in Table 4.6 of the SI.)

Figure 4.2e indicates that 2-stroke SOREs emit more PM than any other source; they emit at least an order magnitude more primary PM than LDGV. Our 2-stroke primary PM estimates are slightly higher than estimates for uncontrolled diesel trucks, the next highest PM source category in our study, but our estimates are lower than those from Volckens et al. The large impact of DPFs on PM from HDDV is evident in this figure; HDDV+DPF emitted two orders of magnitude less PM than uncontrolled HDDV and MDDV. Four-strokes emitted less primary PM than 2-strokes, and though their emission rates were highly variable, the median emissions are comparable to LDGV. Primary PM emissions from the TRU are very similar to the uncontrolled HDDV and MDDV.

The median OC emissions from 2-strokes are significantly greater than all other source categories. The next highest category was 4-strokes, and the median OC values from these 2-

strokes and 4-strokes are 0.73 g-C/kg vs. 0.17 g-C/kg, respectively. This trend is not changed when medians are calculated using only two-strokes and four-strokes tested on cycle C (data not shown): 2-strokes emitted 0.73 g-C/kg and 4-strokes emitted 0.28 g-C/kg of OC. Four-stroke gasoline SOREs are comparable to MDDV, uncontrolled HDDV, TRU and higher or much higher than LDV—the latter of which have reduced OC by an order of magnitude from pre-LEV to LEV-2 models. The DPF-equipped HDDV emit very little OC (some measurements were negative, hence the absence of the lower part of the boxplot for HDDV+DPF), putting them on par with LEV-2 vehicles.

Predictably, the uncontrolled diesel engines (HDDV, MDV and TRU) emitted the highest amounts of EC; while the HDDV+DPF had the lowest EC emissions among all source categories (some measurements were negative, indicating that the levels approached the lower detection limit of the instruments). The median EC values for 2- and 4-strokes differs significantly only when experiments from the same test cycle are compared: two-strokes and four-strokes tested on cycle C emitted median EC values of 0.01 and 0.08 g-C/kg, respectively.

Figure 4.2h indicates the dramatic difference in the OC/EC ratio for 2-strokes compared to all other source categories. Although there is some variability, especially among the LDV, all other categories have OC/EC ratios roughly equal to unity. Four strokes may be slightly higher—with ratios closer to 4—but 2-stroke ratios are almost two orders of magnitude greater than the other categories. It should be noted that because the EC emissions are extremely low in the two SORE2S-2 experiments the EC measurement uncertainty is larger. However, even if there is two times as much EC as reported, the OC/EC ratio for these two 2-stroke experiments would still be ~150 and the median OC/EC ratio of the four 2-stroke experiments would drop

from 150 to 92—still almost two orders of magnitude greater than the median 4-stroke value of 4.3 ± 2.4 .

4.3.2 Secondary Aerosol Production

Figure 4.3 plots time series of particle- and gas-phase species measured during a typical smog chamber experiment (SORE2S-1.1). There are three distinct periods in each experiment. First, emissions are added to the chamber causing concentrations of VOCs, CO₂ and NOx to increase. The second period begins when the engine is shut off at time = -1 hours and the primary emissions were characterized. HONO was added to the chamber at approximately time = -0.9 hours, leading to an increase in NO₂ concentration. Propene was also added in certain experiments to adjust the VOC/NOx ratio. The third period begins when the UV lights were turned on. SOA was quickly generated immediately after the lights were turned on. After 3 hours the wall-loss corrected organic aerosol concentrations increased by roughly a factor of 20 from ~1 μ g/m³ of POA to ~22 μ g/m³ of OA (average of the ω =0 and ω =1 estimates in Figure 4.3c). During the 3 hours of UV irradiation much of the NO and primary hydrocarbons are oxidized to NO₂ and oxygenated VOCs, respectively (Figure 4.3a-b).



Figure 4.2. (a)-(d) Gas- and (e)-(h) particle-phase data measured in the CVS for 10 SORE (six 2-stroke and four 4stroke experiments) and 2 TRU experiments are shown in the shaded region of the panels. Also shown (black filled circles in panels a-e) are data from a SORE 2-stroke study by Volckens et al. [35], and vehicle emission studies by Gordon et al. [6, 7] for comparison. Data from duplicate experiments were averaged before plotting. Only one TRU engine was tested (twice); its values are therefore represented by a single line on the far right side of the two columns of panels. A complete list of all experimental SORE/TRU data (including duplicate experiments) is provided in Table 4.6 of the SI. The central marks on the boxplots are medians, the edges of the boxes are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers (>1.5 x interquartile range) are plotted individually with the "+" symbol.



Figure 4.3. Gas and particle evolution during a typical smog chamber experiment (SORE2S-1.1). Between -1.4 hr < time < -1.0 hr, the chamber was filled with dilute emissions from the backpack blower; for -1.0 hr < time < 0 hr, the primary PM was characterized; for time > 0 hr, the UV lights were on and photo-oxidation generated SOA. Concentrations of NOx, O_3 and CO_2 are shown in (a). Shown in (b) are the concentrations of three VOCs which are consumed by OH radicals during the photo-oxidation period. Shown in (c) are uncorrected and corrected (for wall losses) organic PM concentrations; the large increase is due to SOA production. The organic concentrations were corrected using two different methods (ω =0 and ω =1) which provide an estimate of the uncertainty of the SOA production.

The SOA production measured at the end of the six SORE chamber experiments is plotted in Figure 4.4. These data are after 3 h of photo-oxidation, which generated OH exposures of $1-2x10^7$ molec-hr cm⁻³. This OH exposure corresponds to 3.5-7 hrs of equivalent atmospheric aging at typical summertime OH concentrations of $3-5x10^6$ molec cm⁻³.



Figure 4.4. SOA production as a function of total organic aerosol concentration in six chamber experiments with one 2-stroke and one 4-stroke SORE (four experiments with SORE2S-1 and two experiments with SORE4S-4, respectively). The VOC/NOx ratios ("V/N") are next to each data point. Error bars indicate the range of the SOA estimates using the two different wall loss correction methods (ω =0 and ω =1); the data points are the averages of the range.

As the two "2-stroke CMU" data points show in Figure 4.4, SOA production can vary substantially even for experiments with the same engine and tested at the same facility. However, this variability appears to be largely driven by differences in gas/particle partitioning and VOC/NOx ratio. Following Odum et al. [37], Figure 4.4 plots SOA production as a function of OA concentration in the chamber. The SOA production monotonically increases with OA, demonstrating that the SOA formed is semivolatile [37, 38] and that the increase in production is largely due to changes in gas-particle partitioning. This behavior is commonly observed in smog chamber experiments performed with single precursors [39, 40]. Essentially, increasing the amount of sorptive material drives more semi-volatile material to partition to the particle phase to maintain thermodynamic equilibrium [41, 42]. Thus, in order to represent this effect, the SOA production per mass of fuel is plotted in Figure 4.4 as a function of total organic aerosol

concentration, C_{oa} , in the chamber for each experiment. The large differences between the C_{oa} from different experiments are due to technical difficulties in injecting the same amount of exhaust into the chamber. The 2-stroke CMU experiment with a C_{oa} of 68.5 produced about twice as much SOA as the 2-stroke CMU experiment with a C_{oa} of 22.0.

In addition to the gas-particle partitioning effect, the SOA production may also depend on the VOC/NOx ratio. These ratios are listed next to each data point in Figure 4.4. Within each of the three pairs of data presented in this figure the experiment with the higher VOC/NOx ratio also has the greater SOA production. For example, among the two "2-stroke CMU" data points in Figure 4.4, the experiment with the VOC/NOx ratio of 5.2 produced more SOA than the companion experiment with a VOC/NOx ratio of 2.0. The impact of NOx on SOA formation from the oxidation of precursor VOCs with the hydroxyl radical is complicated [31]. Under high NOx conditions, organo-peroxy radicals (RO₂) react with NO and NO₂ instead of with peroxy radicals (RO₂ or HO₂), which can lead to changes in functionalization and subsequent fragmentation, oligomerization, and isomerisation. Such changes can, in turn, affect vapor pressures of the products and, ultimately, the SOA production [43]. Others have shown a positive correlation between VOC/NOx ratios and SOA production in photo-oxidation studies of both single-component model systems [31, 32] and more complex vehicle emissions [7].

Although experimental difficulties made it impossible to directly verify, Figure 4.4 suggests that SOA production from 2-stroke emissions is significantly greater than from 4-stroke emissions under identical C_{oa} and VOC/NOx conditions. This is not surprising since the NMOG emissions from 2-stroke are so much higher. However, since the 4-stroke experiments had lower VOC/NOx ratios than any of the 2-stroke experiments, it could be argued that the lower production from the 4-strokes is due to the VOC/NOx ratios in the chamber rather than some

intrinsic property of the emissions profiles from the two different SOREs. One of the 4-stroke experiments has a VOC/NOx ratio of 1.7 and a C_{oa} of 16.5, which is smaller, but quite close to the VOC/NOx ratio of 2.0 and a C_{oa} of 22.0 for one of the CMU 2-stroke experiments. Among these two experiments the 2-stroke SOA production was about 6 times higher than the 4-stroke experiment.

The SOA production estimates shown in Figure 4.4 were grouped according to engine type (2- or 4-stroke) and plotted in Figure 4.5c (data are in Table 4.6 and Table 4.7 of the SI) along with the values for a range of vehicular sources. SOA produced from 2-stroke gas-phase emissions are an order of magnitude greater than all other sources measured in this study. This is likely due to the much higher NMOG emissions, as discussed previously in relationship to Figure 3.8. The 4-strokes were the second largest source of NMOG emissions (Figure 4.2d); thus, it is not surprising that it is also the second largest source of SOA.

SOA production relative to POA in the chamber is summarized in Figure 4.5d. The data indicate that the ratio of SOA to POA for 2-strokes is roughly the same as for the newer LDGV (LEV-1 and LEV-2). This reinforces the observation that a lot of SOA forms when the gas-phase emissions from the 2-strokes photo-oxidize because the absolute amount of POA from these engines is also high. The ratio of SOA/POA for 4-strokes is at least an order of magnitude lower than 2-strokes; 4-strokes have one of the lowest SOA/POA ratios of all the sources in Figure 4.5d.

From a policy perspective it is also informative to consider the ratio of SOA to primary PM, for the latter is one of the regulated quantities (POA is not regulated). The rankings for the off-road engines changes somewhat when SOA is compared to primary PM instead of POA.

Two-strokes, while no longer the highest source, are comparable to a wide range of LDGV when using SOA/primary PM as the metric.

4.4 Conclusions

The first goal of this study was to improve our understanding of the primary gas- and particle-phase emissions from a variety of common, small off-road engines (SORE) and a diesel transportation refrigeration unit (TRU). The second goal was to characterize the SOA production that occurs when gas-phase emissions from SORE are photo-oxidized under urban-like conditions in a smog chamber. While SOREs are generally smaller than car and truck engines and they are responsible for only about 0.5% of the fuel consumption, they are a ubiquitous source—some 100 million SOREs are sold per year globally [4]. Given their wide use, reportedly high emissions, and the fact that they emit their exhaust in close proximity to the operator (e.g., a lawnmower, as opposed to a car), it is important to understand their impact on air quality.

SORE emissions—especially those from 2-stroke gasoline engines—were found to have much higher levels (per mass of fuel consumed) of NMOG, primary PM and organic carbon than the other reference sources (a variety of different gasoline cars and diesel trucks). Our 2-stroke primary measurements were in excellent agreement with data from another study of 2-stroke leaf blowers [35]; where the numbers from the two studies differed, ours were typically slightly lower (e.g., NMOG and primary PM).

The 2-stroke NMOG emissions were more than an order of magnitude larger than NMOG from pre-LEV vehicles, presumably due to the well-known tendency for these engines to emit unburned fuel along with the exhaust [44, 45]. In this work we tested four different 4strokes, and the emissions from them varied significantly (as much as two orders of magnitude for some emission factors). (The same may be true for 2-strokes, but we only tested two of these.) Comparing median values, pollutant concentrations from 4-stroke gasoline engines was lower than 2-strokes, but 4-stroke emissions are still at least as high and in several cases considerably higher than those from the oldest gasoline vehicles (pre-LEV) currently on the road (e.g., median 4-stroke NMOG value was 2-3 times greater). The diesel TRU emission factors for most primary pollutants were very similar to those of diesel trucks.

OC emissions from 2-strokes are an order of magnitude higher than all the other reference categories. Four-stroke OC emissions are lower than 2-stroke but still much higher than pre-LEV gasoline vehicles. The OC/EC ratios for 2-stroke SOREs are dramatically higher than all other sources. Together, these facts reinforce the clear distinction between gasoline vehicles and gasoline off-road devices.

Photo-oxidation of dilute 2-stroke SORE emissions produces more SOA than any other source, followed by 4-strokes. These rankings are not surprising given the very high NMOG emissions of the 2- and 4-strokes. (SOA production for the TRU was not measured.) Relative to primary PM, 2-strokes produce roughly as much SOA as LDGV, and 4-strokes, with their higher EC emissions, have SOA/primary PM ratios that are comparable to diesel vehicles.

In summary, we find, in keeping with previous studies, that off-road gasoline engines emit large amounts of gas-phase pollutants and primary PM relative to the amount of fuel that they consume. Our coverage of off-road diesel engines (TRU) was restricted to one TRU—an older model without a diesel particulate filter or other aftertreatment device. The emission profile of the TRU was much like the diesel engines found on a variety of trucks to which it was compared; it emitted high amounts of EC and OC but relatively little NMOG. SOA production from the SOREs was also high, both on an absolute mass basis (per mass of fuel consumed) and relative to the amount of primary PM that they emit. Thus, in addition to the large amount of PM emitted directly from the tailpipe of these engines, a large amount of additional secondary PM is very rapidly formed when the gas-phase emissions are exposed to atmospherically relevant conditions. Indeed, with 2-strokes, SOA increases the net PM mass by a factor of 2 or 3 after only 3 hours of oxidation. Given the fact that photo-oxidation is likely to continue for many additional hours in the atmosphere [46, 47], the net PM from these engines could be much larger than what we have estimated here. This result strongly suggests the need to more carefully assess their contribution to the total pollutant burden emitted by the full range of combustion sources operating within a given region.



Figure 4.5. Particle-phase data for all the combustion sources tested in the smog chamber. (a) primary organic aerosol measured in the chamber, (b) total primary PM mass measured with gravimetric analysis of Teflon filters collected in the CVS following CFR 1065 procedures, (c) SOA measured in the chamber, (d) ratio of SOA to POA and (e) ratio of SOA to primary PM. Data for 2-stroke SOREs and 4-stroke SOREs (in blue shaded area), light-duty gasoline vehicles (LDGV), medium-duty diesel pick-up trucks (MDDV), and heavy-duty diesel vehicles with and without a DPF (HDDV+DPF, HDDV). Chamber experiments were not performed with the TRU. Data from duplicate experiments were averaged before plotting. The central marks on the boxplots are medians, the edges of the boxes are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers (>1.5 x interquartile range) are plotted individually with the "+" symbol.

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4.6 Supplemental Information

	C 4	C₅	C ₆	C ₇	C ₈	C₅	C ₁₀	C ₁₁₊				
paraffins	0.69	9.12	11.45	11.62	12.8	3.05	1.27	2.29				
aromatics			0.66	6.12	10.17	8.32	2.14	0.9				
cyclic olefins		0.08	0.26	0.19	0.06	0.01						
olefins/naph- thalenes	12.38											
polynaph- thalenes	0.22 6.2											
МТВЕ												
TOTAL (mass%)	100% = 84.97% C + 13.91% H + 1.12% O											

Table 4.5. Chemical analysis of gasoline used in all spark-ignition SORE experiments, listed as mass percentages for compounds with 4 or more carbon atoms.

Table 4.6. Gas-phase and primary particle-phase emissions as measured in the CVS for all SORE and TRU experiments performed at HSL, including duplicate experiments ("dup. expt" in table). These data are summarized graphically in Figure 4.2.

	test date	expt ID	dup. expt	fuel	тнс	со	CO2	CH4	NOx	NO	ос	EC	OC/EC	PM
				(kg)	(g/kg)		(g/kg)							
e	2/2/2012	SORE2S-1.1		0.309	119.7	567	1850	5.9	0.51	0.04	0.472	0.016	29.7	?
ð	2/3/2012	SORE2S-1.2	У	0.315	116.0	563	1867	5.8	0.48	0.00	0.557	0.016	34.8	?
-sti	2/10/2012	SORE2S-2.1		0.078	239.4	531	1530	2.2	1.83	0.66	1.150	0.004	274.2	?
2	2/10/2012	SORE2S-2.2	у	0.079	240.4	547	1501	2.2	1.75	0.57	0.739	0.002	305.1	?
	2/9/2012	SORE4S-1.1		0.373	10.7	426	2413	1.0	14.3	8.62	0.015	0.003	4.3	?
e	2/9/2012	SORE4S-1.2	У	0.382	10.9	472	2340	1.1	13.0	7.84	0.012	0.003	4.1	?
ğ	2/13/2012	SORE4S-2.1		0.056	44.3	368	2400	3.0	15.6	9.80	0.178	0.021	8.4	?
-st	2/13/2012	SORE4S-2.2	У	0.056	44.5	360	2412	3.1	19.7	12.4	0.170	0.024	7.0	?
4	2/15/2012	SORE4S-3.1		0.263	6.95	342	2558	0.7	21.5	13.3	n/a	n/a	n/a	?
	2/16/2012	SORE4S-4.1		0.273	22.80	648	2027	2.2	6.2	4.0	0.487	0.1960	2.48	?
⊋	2/8/2012	TRU4S-1.1		1.13	2.75	7.00	3097	0.0	29.8	17.4	0.205	0.117	1.7	?
Ħ	2/8/2012	TRU4S-1.2	У	1.12	2.90	7.15	3096	0.1	29.6	17.2	0.218	0.110	2.0	?

Note OC/EC instrument uncertainty for EC>100% in the shaded box (SORE2S-2.2).

Table 4.7. Particle-phase (POA, SOA, BC and inorganic seed) and gas-phase (NOx, propene, butanol and NMOG) concentrations and/or emission factors in the smog chamber during the seven SORE 2-stroke and 4-stroke chamber experiments. Also included at the bottom of the table are the chamber conditions during a dynamic blank experiment in which only CVS air with no exhaust is injected into the chamber and photo-oxidized.

	test date	expt ID	test cycle	dup. expt	VOC/ NOx	seed?	POA (g/kg)	avg SOA (g/kg)	avg C _{OA} (µg/m³)	BC (μg/m³)	NO (ppb)	NO ₂ (ppb)	propene (ppm)	butanol (ppm)	NMOG (ppmC)
sts	2/2/2012	SORE2S-1.1	Cyclo C		11.66	no	0.041	0.915	22.6	0.2	235	380	0	0.057	2.11
iL te	2/3/2012	SORE2S-1.2	Cycle C	у	2.94	no	0.051	0.255	6.0	0.2	636	282	0	0.057	2.22
HS	2/16/2012	SORE4S-4.1	Cycle C		2.95	no	+	+	+	2.9	110	124	0.130	0.057	0.95
tests	5/9/2012	SORE2S-1.3	mod.		5.18	no	0.072	1.457	68.5	n/a	399	856	0	0	n/a
	6/13/2012	SORE2S-1.4	Cycle C	У	2.01	no	0.142	0.780	22.0	n/a	535	1295	0	0	n/a
MU	5/14/2012	SORE4S-4.2	mod.		1.32	no	0.355	0.098	7.3	n/a	840	596	0	0.100	n/a
0	6/6/2012	SORE4S-4.3	Cycle C	у	1.65	no	0.184	0.128	16.5	n/a	818	829	0	0.100	n/a
blnk	2/9/2012	dyn. blank	0.5 h CVS		2.86	yes	n/a	0*	0*	0.3	63	153	0.130	0.057	0.71

*AMS data were not available during the blank experiment, but SMPS data indicate no increase in PM mass during photo-oxidation. † AMS was offline for this experiment.

Chapter 5: Synthesis, Conclusions and Policy Recommendations

This chapter begins with a summary of the key findings from the experiments with gasoline light-duty vehicles (Chapter 2), medium- and heavy-duty diesel vehicles (Chapter 3) and small off road engines and transportation refrigeration units (Chapter 4). It then presents fuel consumption data for on- and off-road sources in the South Coast Air Basin (of southern California) predicted by two different emissions/fuel consumption models developed by the California Air Resources Board and uses these data in conjunction with the experimentally-derived primary PM emission factors and SOA production factors (i.e., primary PM and SOA per mass of fuel consumed) to estimate the regional contribution of emissions from these sources to fine PM. The objective of the second part of this chapter is to put the experimental work in context by shifting the focus from the emissions and SOA production of individual sources to a more holistic picture of PM pollution from all on- and off-road combustion sources that may be useful to policymakers. Policy recommendations are summarized in the final section of this chapter.

5.1 Summary of Key Findings in This Work

The research described in this dissertation demonstrates the importance of secondary organic aerosol (SOA) produced from photo-oxidation of gas-phase emissions from a variety of ubiquitous combustion sources. Support for this conclusion was obtained during three field

studies in Los Angeles, undertaken in collaboration with the California Air Resources Board. The experiments provide some of the first direct evidence that SOA has a significant role in total (primary plus secondary) PM production from both on-road and off-road sources.

The overall objective of the experimental work was to characterize primary gas- and particle-phase emissions and SOA production from an array of combustion sources. The core experimental results of this research can be succinctly summarized in two figures. Figure 5.1 presents the primary gas- and particle-phase emissions from all the sources (as measured in the constant volume sampling system, CVS) tested in the three field campaigns, and Figure 5.2 presents the SOA production factors for all the smog chamber experiments and their ratios with total primary PM and with POA. (Though both Figure 5.1e and Figure 5.2b plot primary PM, the former contains measurements in the CVS from primary tests *and* chamber tests, while the latter includes PM measurements in the CVS from the chamber tests only.) Important conclusions for each of the preceding chapters are described in the following sections by reference to Figure 5.1 and Figure 5.2.

5.1.1 Light-duty Gasoline Vehicles (LDGV)

The first major objective of this research was to characterize the primary PM emissions from passenger vehicles and the SOA produced during photo-oxidation of their gas-phase emissions. This study investigated a wide enough range of light duty gasoline vehicles (LDGV) to reasonably represent the existing on-road fleet. Sixty-four LDGV were recruited from the California in-use fleet for primary emissions testing. SOA production from the gas-phase emissions from 15 of these vehicles was also characterized, and the data are presented in detail in Chapter 2. The 15 vehicles used in the smog chamber studies spanned a range of types (cars, SUVs, minivans), model years (1987-2011) and emission standards (pre-LEV, LEV-1 and LEV-2); they were tested over a realistic urban driving cycle (the Unified Cycle). They all used the same summertime commercial California fuel, and a detailed analysis is included in the appendix for chapter 2.

Although there is significant vehicle-to-vehicle variability in primary emissions, the data from chapter 2, summarized in the left 3 data sets in each of the 8 plots in Figure 5.1, indicate that for the overall fleet (64 vehicles), there is a substantial reduction in most primary emissions for newer vehicles that meet more stringent emission standards. This trend holds for gas-phase pollutants including CO, NOx and NMOG (Figure 5.1a, b, d) as well as for primary PM mass and organic carbon (Figure 5.1e-f). Elemental carbon (Figure 5.1g), on the other hand, has not changed significantly since the pre-LEV period. Therefore, the decline in OC/EC ratio for newer LDGV shown in Figure 5.1h is a direct result of reductions in OC.

Broadly speaking, much of the primary emissions characterization described above corroborates numerous previous vehicle emissions studies [1-4]. The primary original contribution of this dissertation is the SOA production results. In the atmosphere SOA is produced when primary emissions are exposed to sunlight, other pollutants, and atmospheric oxidants such as ozone (O₃), the hydroxyl radical (OH), and the nitrate radical (NO₃). Understanding the atmospheric transformation and ultimate fate of gas-phase emissions is critical for quantifying the contribution of a combustion source to ambient PM. However, the SOA produced from LDGV emissions (or emissions from MDDV, HDDV, SORE or TRU) has not been studied previously.

In this research we found that three hours of photo-oxidation of LDGV dilute tailpipe emissions inside the smog chamber under urban-like conditions (i.e., atmospherically relevant OH and primary particle concentrations and somewhat higher NOx and organic gas concentrations) produced large amounts of SOA on both an absolute mass basis (Figure 4.5c) and relative to primary PM and POA emissions (Figure 4.5d-e). For example, the median SOA mass was 2 and 8 times greater than the primary PM (measured in the constant volume sampling system, CVS) for LEV-1 and LEV-2 vehicles, respectively. It is important to note that after being injected into the smog chamber a large fraction of the primary PM measured in the CVS partitions to the gas-phase (in order to maintain thermodynamic equilibrium in the chamber where organic aerosol concentrations are much lower than in the CVS); thus, our SOA/primary PM ratio probably underestimates the ratio that would be measured in the atmosphere, since this change in concentration from the CVS to the smog chamber does not exist there. Furthermore, there is no evidence that SOA production was complete in these experiments after 3 hours (i.e. SOA was still being produced when we ended the experiments); therefore, the emissions are expected to undergo substantially more oxidation, producing even more SOA than we observed in these experiments and increasing the SOA/primary PM ratios. Other studies have shown that SOA production downwind of urban areas may persist for 48 hours [5, 6].

The median pre-LEV vehicle emits much more primary PM than median LEV-1 and LEV-2 vehicles. Thus, while the absolute SOA production for pre-LEV vehicles is high, the relative amount of SOA associated with pre-LEV vehicles is lower than the relative amount of SOA for newer LEV-1 and LEV-2 vehicles. SOA increased the net PM from pre-LEVs by about 80% (rather than by a factor of 2 to 8 as with the LEV-1 and LEV-2 vehicles) when added to their primary PM emissions. These data indicate that SOA formation from LDGV is substantial relative to their primary PM emissions, especially for newer vehicles. The second part of this

chapter will investigate whether SOA is important in the context of all on- and off-road combustion sources.

Despite the large decrease in NMOG emissions for newer vehicles (LEV-2 < LEV-1 < pre-LEV), the SOA production from all three classes of vehicles was comparable on an absolute basis. On average, there appears to be little difference between the amounts of SOA produced from older vehicles or newer ones despite the more sophisticated emissions control systems in the latter. Although a number of factors influence SOA formation (VOC/NOx, C_{OA} , oxidant exposure), these factors did not systematically vary by vehicle class and thus do not seem to explain the differences in the data. Therefore, the data suggest that the organic gas emissions from LEV-2 vehicles may be more efficient SOA production may be relatively more important than primary PM emissions from LEV-2 vehicles in the context of ambient PM.

The effective SOA yields from the different vehicles were estimated by dividing the measured SOA production by an estimate of the NMOG that reacted during the photo-oxidation period of the chamber experiments. For LEV-1 and LEV-2 vehicles traditional SOA precursors (mainly single-ring aromatics) could only explain less than half of the measured SOA production. Therefore, some of the unspeciated NMOG (i.e., organic compounds which the gas-phase instruments could not individually identify) must be important SOA precursors. When the unspeciated NMOG mass was included in the analysis, effective SOA yields were found to decrease in the order LEV-2 > LEV-1 > pre-LEV, and the median values for the different classes of LDGV were 34%, 22% and 1.3%, respectively. The exact species responsible for these differences remain unknown. Differences in semivolatile and intermediate-volatile organic compound mass measured using TD-GC-MS analysis of Tenax sorbent samples do not appear to

explain the variations in SOA. However, the TD-GC-MS analysis targets non-polar and lowpolarity components of the emissions. The SOA precursors may be more oxygenated and therefore poorly detected by the current sampling/analysis approach.

5.1.2 Medium- and Heavy-Duty Diesel Vehicles (MDDV and HDDV)

The second major objective of this dissertation was to characterize the primary PM emissions from diesel vehicles and the SOA produced during photo-oxidation of their gas-phase emissions. Two different medium-duty diesel pick-up trucks (MDDV) and three heavy-duty diesel vehicles (HDDV) were tested, comprising a range of emission control systems (none, DOC, DOC+DPF, DOC+DPF+SCR), fuel types (biodiesel and low-, medium- or high-aromatic ULSD) and test cycles (UC, UDDS, creep/idle, forced DPF regeneration). Vehicles with a diesel particulate filter and diesel oxidation catalyst (DOC+DPF) emitted very little BC and POA. As shown in Figure 5.2d, median NMOG emissions from the MDDV and the uncontrolled HDDV were comparable to emission levels from the lower-emitting LDGV per mass of fuel consumed. For HDDV with DPF aftertreatment, both NMOG and primary PM emissions were close to or below the detectible limit. Primary PM for DPF-equipped HDDV was at least an order of magnitude lower than the next cleanest source (the LEV-2 vehicles). Median OC levels for the DPF-equipped HDDV and for the LEV-2 vehicles are significantly lower than for any of the other sources; the two are comparable and close to the detection limit of the instruments. Median EC emissions from the uncontrolled HDDV and the MDDV were higher than all other sources tested in this research; they were 1-2 orders of magnitude higher than median LDGV levels.

Emissions from the two DPF-equipped diesel vehicles were photo-oxidized in the smog chamber for three hours, but they produced much less (or no measurable) secondary organic aerosol (SOA) compared to vehicles without aftertreatment. However, the DPF-equipped vehicles emitted significant BC, POA and sulfate during forced DPF regeneration experiments. There was also measurable SOA production from the regeneration emissions. For both MDDV and HDDV without aftertreatment substantial SOA formed-with the emissions from some vehicles generating twice as much SOA as POA after three hours of photo-oxidation. For the HDDV without a DPF the SOA yield (estimated from the calculated oxidation of speciated nonmethane organic precursor gases) was approximately 10%. While net PM (primary+secondary) and POA were comparable for the 3xcreep+idle cycle and higher speed urban operation (UDDS), SOA production from 3xcreep+idle cycle was 3-4 times larger than SOA production from the UDDS cycle. This increase in SOA production from 3xcreep+idle emissions was offset by lower BC emissions. Figure 4.5c shows that on an absolute mass basis SOA production from the uncontrolled (no DPF) diesel vehicles' emissions was comparable to SOA produced from photooxidized LDGV emissions; however, due to the very high EC emissions of these vehicles the ratio of SOA to primary PM is lower than for LDGV (Figure 4.5e) after three hours of photooxidation.

Although the aromatic emissions from HDDV was positively correlated with the aromatic content of the three different ULSDs fuels, this variable had no effect on primary PM or SOA production. With the MDDV, switching from ULSD to biodiesel reduced BC substantially while leaving POA and SOA unchanged. Although SOA production from diesel- and biodieselfueled vehicles without a DPF was significant on an absolute basis, the net PM from these vehicles was dominated by BC.

5.1.3 Off-road Engines (SORE and TRU)

The third objective of this research was to characterize the primary PM emissions from a variety of small off-road engines (SORE) and a diesel engine used to power a transportation refrigeration unit (TRU). In addition, the SOA produced during photo-oxidation of the gas-phase emissions from two of these sources was characterized in smog chamber experiments. Sixteen SORE/TRU experiments were conducted including nine primary tests in which only primary PM and gases were characterized and seven chamber tests in which SOA formation were measured (in three of these seven chamber experiments NMOG was measured in the CVS).

NMOG emissions for the 2- and 4-stroke SORE were greater than any other source tested in this work (Figure 5.1d). The 2-stroke NMOG emissions were more than an order of magnitude larger than NMOG from the pre-LEV vehicles, presumably due to the well-known tendency for these engines to emit unburned fuel along with the exhaust [7, 8]. The median 4stroke NMOG value was 2-3 times greater than the next highest source, the pre-LEV vehicles. The 2-stroke data were found to be in excellent agreement with the results from a SORE 2-stroke study by Volckens et al. [9].

Although the OC and EC emissions (Figure 5.1e-f) of the 4-strokes are quite variable (spanning two orders of magnitude), the median OC emissions from 2-strokes is significantly greater than all other source categories. Four-stroke OC emissions are comparable to MDDV, uncontrolled HDDV, TRU and higher or much higher than LDGV. Figure 5.1h indicates the dramatic difference in the OC/EC ratio for 2-stroke SOREs compared to all other source categories. Although there is some variability, especially among the LDGV, the OC/EC ratios for all other sources are roughly equal to unity, with gas and diesel vehicles falling between 0.1

and 1 and off-road four-strokes closer to 4. OC/EC ratios for 2-strokes are almost two orders of magnitude greater than the other source categories. The primary gas- and particle-phase data obtained from the 2-strokes were found to correlate well with a previous study [9] conducted with a set of three leaf blowers similar to the ones we tested (data shown in chapter 4 only).

On an absolute basis, photo-oxidation of dilute 2-stroke SORE emissions produces more SOA than any other source (Figure 4.5c), followed by 4-strokes. This is not surprising given the very high NMOG emissions of the 2-strokes. (SOA production for the TRU was not measured.) Relative to primary PM, 2-strokes produce as much SOA as LDGV, and 4-strokes, with their higher EC emissions, have SOA/primary PM ratios that are comparable to diesel vehicles.



Figure 5.1. Primary (a)-(d) gas- and (e)-(h) particle-phase emissions measured in the CVS for all the combustion sources tested for this dissertation. The on-road gasoline vehicle data (3 red-shaded data sets on left) were presented in detail in chapter 2; the on-road medium- and heavy-duty diesel truck data (3 green-shaded data sets in middle) in chapter 3; the off-road 2- and 4-stroke gasoline SOREs and the TRU (3 blue-shaded data sets on right) in chapter 4. Data from duplicate experiments were averaged before plotting. Only one TRU engine was tested (twice); its values are therefore represented by a single line on the far right side of the two columns of panels. The central marks on the boxplots are medians, the edges of the boxes are the 25th and 75th percentiles, the whiskers extend to the most



extreme data points not considered outliers, and outliers (>1.5 x interquartile range) are plotted individually with the "+" symbol.

Figure 5.2. Particle-phase data for all the combustion sources tested in the smog chamber. (a) primary organic aerosol measured in the chamber, (b) total primary PM mass measured with gravimetric analysis of Teflon filters collected in the CVS following CFR 1065 procedures, (c) SOA measured in the chamber, (d) ratio of SOA to POA and (e) ratio of SOA to primary PM. The on-road gasoline vehicle data (3 red-shaded data sets on left) were

presented in detail in chapter 2; the on-road medium- and heavy-duty diesel truck data (3 green-shaded data sets in middle) were in chapter 3; the off-road 2- and 4-stroke gasoline SOREs (2 blue-shaded data sets on right) were in chapter 4. Data from duplicate experiments were averaged before plotting. The central marks on the boxplots are medians, the edges of the boxes are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers (>1.5 x interquartile range) are plotted individually with the "+" symbol.

5.2 Combining Emissions Profiles and Fuel Consumption

Data

The foregoing summary of the conclusions from the experimental studies showed that with certain combustion sources SOA production inside a smog chamber is very large relative to primary emissions after only three hours of photo-oxidation under urban-like conditions. With LEV-2 LDGV, for example, the measured SOA is 8 times larger than primary PM for the median vehicle. While such conclusions are useful, to develop effective control strategies it is important to consider the total amount of PM produced in aggregate by all the various combustion sources operating in a given region. We now turn to that task, presenting analysis for California's South Coast Air Basin (SoCAB). SoCAB, which includes non-desert portions of Los Angeles, Riverside and San Bernardino counties, comprises 6,745 square miles and 16.8 million people about half the population of California; it is the second most populated urban area in the United States and is plagued by particularly poor air quality. PM10 levels in SoCAB exceeded the allowable national annual average (50 μ g/m³) every year between 1990 and 2006. In 2006 this standard was revoked and replaced by a 15 μ g/m³ PM2.5 national standard [10]. SoCAB has been in violation of the PM2.5 standard since its adoption (California Air Resources Board, http://www.arb.ca.gov/adam/welcome.html). Furthermore, studies have shown that SOA

constitutes up to 80% of total ambient organic PM in SoCAB [11], and the overwhelming majority of the SOA precursors in SoCAB are emitted by anthropogenic sources [12]. We obtained three different estimates for aggregate PM emissions in SoCAB: (1) predicted primary PM using CARB emission models (EMFAC and OFFROAD), (2) predicted primary PM from CARB plus an estimate of SOA production based on data from this study and (3) primary PM emission and SOA production measured by this study multiplied by fuel consumption. These estimates are referred to as (1) "CARB primary PM," (2) "CARB primary PM+SOA" and (3) "PM production times fuel." The methods used to obtain these three estimates are presented, and then the results are compared.

First, to generate the "CARB primary PM estimate," CARB's EMFAC model [13] and OFFROAD model [14] were used to estimate primary PM emissions in 2010 (SOA is not accounted for by either model) for all on-road vehicles and off-road sources (commercial aircraft, marine vessels and locomotives are not included in the models or this analysis), respectively. These models use emissions data generated by the certification test procedures for exhaust (and evaporative emissions). For EMFAC the exhaust emissions are based on a standard certification driving cycle such as the UC (used with the LDGV tested in the current research), which includes cold start, hot-stabilized driving, and hot start. EMFAC and the U.S. EPA's MOBILE model are the two most widely used on-road emissions models in the U.S. The EMFAC model assigns model-year specific, emission rates to each class of vehicles. For post-1981 LDGV the rate is adjusted to reflect the number of vehicles with carburetors, fuel injection, or other relevant engine/emissions controls [15]. A deterioration rate is then applied to the emissions as a function of mileage. To account for the fact that some vehicles experience malfunctions or tampering that increase emissions, a percentage of the fleet (which increases with vehicle age) is modeled as high-emitters [16]. The OFFROAD model (similar to the U.S. EPA's NONROAD model) is structured similarly to EMFAC. OFFROAD generates emission inventories by equipment type, accounting for age, growth/scrappage, seasonal/temporal patterns, deterioration, temperature and relative humidity [17].

The "CARB primary PM" estimates are shown graphically in Figure 5.3 and in column 10 of Table 5.1. In Figure 5.3 the 22.2 tons of PM/day predicted by this estimate is divided among five categories based on (1) fuel type (gasoline or diesel), (2) operating domain (on-road or off-road) and (3) engine configuration (2-stroke or 4-stroke). In Table 5.1 the on-road categories are divided into additional subgroups based on aftertreatment type (DPF/no DPF for diesel on-road sources) and emission standard (pre-LEV, LEV-1 and LEV-2 for gasoline on-road sources).

The second and third estimates of aggregate PM emissions were calculated using the gasoline and diesel fuel consumption and the primary PM emissions and SOA production data measured in this study. Fuel consumption data were obtained from EMFAC and OFFROAD; they predict that 23.4 million gallons of fuel/day were consumed in SoCAB in 2010. Figure 4 shows the breakdown of fuel usage into the same five primary categories used in Figure 5.3. These data are also tabulated in column 6 of Table 5.1.

There are striking differences between the PM emissions predicted by "CARB Primary PM" in Figure 3 and the fuel consumption in Figure 5.4. 65% of all fuel (79% of the 82.7% consumed by on-road gasoline) is consumed by LDGV, but EMFAC predicts that only about 6% of the total PM emissions is from LDGV. On-road diesel sources use about 9% of the fuel in SoCAB, with HDDV (type 3 trucks) similar to those described in chapter 3 consuming the majority of that fraction. Despite their relatively modest fuel consumption, type 3 trucks are

responsible for 22% of the predicted PM emissions from on- and off-road sources, according to the "CARB Primary PM" estimate in Figure 3. Off-road diesel sources consume about half as much fuel as on-road diesel and most of that fuel is used by construction and mining equipment. Diesel TRU, such as the one described in chapter 4, consume only about 7% of the 5.7% attributed to off-road diesel, or about 0.4% of the total fuel consumed in SoCAB. Off-road 4strokes are not dominated by any single source category; lawn and garden equipment, including devices such as the 4-stroke blower discussed in chapter 4, use approximately the same amount of fuel as TRU in aggregate. Among 2-stroke gasoline engines, pleasure craft (e.g., private motorized boats) use the majority of the fuel, but the absolute amount of fuel consumed by engines in this category is very small. Together all 2-strokes are estimated by the OFFROAD model to use about the same amount as the TRU. Two-stroke lawn and garden equipment (e.g., the 2-stroke blower described in the smog chamber experiments in chapter 4) consume only 0.1% of all fuel in SoCAB. In spite of the fact that 2-strokes consume such little fuel overall, Figure 5.3 indicates that they are predicted to be the third highest PM emitter of all the source categories, according to the "CARB Primary PM" estimate.

The distribution of fuel consumption (Figure 5.4) is reasonably mirrored by the number and variety of experiments performed for this dissertation research. For example, the source category responsible for the majority of the fuel consumption, LDGV, is also the one for which we have the greatest number of experiments and the most variety of vehicle types. The next largest category in terms of fuel consumption is type 1 (light-duty) gasoline trucks. This category includes vehicles < 14,000 pounds, some of which were tested in the LDGV portion of this research (e.g., pickups and SUVs), and we assume for this analysis that the emissions from all the vehicles in this category are similar to LDGV. Type 3 trucks consume the next largest amount of fuel, and, although we did not test a large number of trucks, the three that were tested span the range of existing types. With these trucks we performed extensive duplicate experiments and investigated fuel effects in detail. Furthermore, our results with DPF-equipped HDDV are in excellent agreement with many previous studies that report >90% reductions in primary PM from both heavy-duty [18-20] and medium-duty [21, 22] DPF-equipped diesel engines.

There is a much greater variety of off-road sources with very different emissions properties. Emissions from these categories are difficult to accurately assess based on the few devices we tested. In addition, there is substantial uncertainty in off-road inventories. For example, Millstein and Harley found that CARB's OFFROAD model predicted over 3 times more PM than the fuel-based estimates they developed [23]. On a national level a similar discrepancy between PM estimates from the EPA's NONROAD model (for off-road sources) and a fuel based prediction have been reported [24]. The emissions properties of construction/mining equipment, which is responsible for the largest fuel consumption among offroad subcategories, are likely very different than leaf blower or TRU emissions. Thus, although we tested at least one engine from each of the five categories shown in the fuel consumption diagram (Figure 5.4), our coverage of the off-road categories is much less representative of the actual variety of sources in use than our coverage of on-road sources.



Figure 5.3. The "CARB Primary PM" estimate for 2010 PM emissions in SoCAB, obtained from the EMFAC and OFFROAD models. Total PM is slightly higher here than in Table 5.1 because some minor contributors were excluded from the latter estimate. The color scheme representing the different categories and subcategories matches that used in Figure 5.4 to facilitate easy comparison between fuel consumption from a particular source and the corresponding PM production estimated by the models. LDV=light duty vehicle (passenger cars, SUVs and pick-up trucks weighing less than 5750 lb), TRU=transportation refrigeration unit (used to cool perishable cargo during transport), rec. equip=recreational equipment (e.g., snowmobiles, ATVs). Larger trucks are classified by weight: type 1 trucks (5751-14,000 lbs), type 2 trucks (14,001-33,000 lbs), type 3 trucks (>33,000 lbs).

The median production of both primary PM and SOA, which were shown graphically in

Figure 5.1 and Figure 5.2, are compiled in columns 4 and 5 of Table 5.1, respectively. As previously indicated, the PM production from the off-road sources is poorly represented by the set of sources tested during this study. Lacking further experimental data, we assume that all 2-

stroke gas engines are represented by the two devices that we tested (a leaf blower and a string trimmer); only the blower was tested in the smog chamber. The 4-stroke gas primary PM emission factor is derived from 4 different devices, but all of these were from the lawn/garden category, which comprises a minority of the fuel use in the 4-stroke gas off-road class. Furthermore, the SOA formation from only one of these devices was tested in the smog chamber. We did not perform any chamber experiments with off-road diesel sources, so we assume that they produce comparable amounts of SOA (on a fuel basis) to on-road uncontrolled HDDV. The facts that OC and (to a lesser extent) NMOG emissions from the two types of diesel sources were roughly equal provide some support for this assumption; however, the only off-road diesel tested was the TRU. Using these assumptions and the fuel consumption data, we calculate the primary PM and SOA (tons/day) shown in columns 8 and 9 in Table 5.1; these values comprise the "PM production times fuel" estimate.

Table 5.1. Median primary PM and SOA production (per mass of fuel consumed in columns 4-5) compiled from chapters 2-4 of this research are multiplied by fuel consumption (in millions of gallons/day in column 6) in the South Coast Air Basin to obtain the calculated primary PM emissions and SOA production (in tons/day in columns 8-9) in the region. The modeled emissions were calculated for the year 2010 using CARB's OFFROAD and EMFAC models for off-road and on-road sources, respectively. Notes: (1) all off-road diesel sources are assumed to have the same emission/production factors as the median uncontrolled (no DPF) on-road HDDV; (2) 32% of HDDVs (i.e., MY2007+) have DPFs, 68% do not and all other on-road diesels (including buses) are assumed to have DPFs in the same proportion.

		_	col. 4	col. 5	col. 6	col. 7	col. 8	col. 9	col. 10	col. 11
			PM production per mass of fuel		fuel consumption in SoCAB		fuel x Р _{prim_PM}	fuel x P _{SOA}	CARB modeled emissions	
col. 1	col. 2	col. 3	P _{prim_PM} (g/kg)	P _{SOA} (g/kg)	fuel (10 ⁶ gal/d)	fuel (%)	prim. PM (ton/d)	SOA (ton/d)	prim. PM (ton/d)	notes
off-road sources	2-str. gas		0.876	0.848	0.09	0.4%	0.24	0.23	3.71	
	4-str. gas		0.060	0.190	0.43	1.8%	0.08	0.24	1.72	
	diesel		0.414	0.098	1.34	5.7%	1.66	0.39	9.40	1
on-road sources	diesel	HDDV+DPF	0.000	0.000	0.69	2.9%	0.00	0.00	0.26	2
		HDDV	0.641	0.098	1.52	6.5%	2.93	0.45	5.29	2
	gas	pre-LEV	0.061	0.069	1.81	7.7%	0.33	0.38	0.63	
		LEV-1	0.020	0.066	7.08	30.2%	0.43	1.40	0.61	
		LEV-2	0.019	0.051	10.48	44.7%	0.60	1.61	0.05	
TOTAL			n/a	n/a	23.44	100%	6.27	4.70	21.68	

Figure 5.5 displays the different PM emissions estimates from Table 5.1 in a graphical format that facilitates comparison between the different estimates on both an absolute and a relative basis. Figure 5.5 presents (1) "CARB Primary PM," i.e., predicted emissions from EMFAC and OFFROAD shown in column 10 of Table 5.1; (2) "CARB primary PM+SOA," i.e., the sum of the CARB predicted primary emissions plus an estimate of the SOA production based on the data reported here (sum of columns 8 and 9 in Table 5.1); and (3) "PM production times fuel," i.e., the primary PM emission factor and the SOA production factor (based on the measurements from this research) scaled with ARB fuel estimates (sum of columns 9 and 10 in Table 5.1).

Figure 5.5 indicates that SOA has the largest impact for the LDGV categories (pre-LEV, LEV-1 and LEV-2). Based on the "CARB primary PM" estimate, which does *not* include SOA, the LDGV are not among the most important PM sources; the ranking from this model is: off-road diesel > on-road diesel > off-road 2-stroke gasoline. Combining all three subgroups of LDGV and using the "CARB primary PM+SOA" estimate, which includes SOA production, the

three most important categories of net PM production are off-road diesel > on-road diesel > LDGV. Switching to the "PM production times fuel" estimate shifts the importance of LDGV even higher. This switch, which replaces the CARB modeled primary PM with the primary PM estimated from the emission factors measured in this study and the fuel consumption data, the PM ranking becomes LDGV > on-road diesel > off-road diesel.

All three PM estimates agree that HDDV represent a large source of PM (second highest source in all three estimates), and Figure 5.5 shows that SOA is a significant contributor for the uncontrolled HDDV. Diesel off-road sources are also important according to all estimates, although the exact ranking varies.

The significant differences in ranking of the sources are primarily due to the previously mentioned difference in the off-road diesel PM estimated from the models and from the emission factors. Without further information about the accuracy of the database used by the OFFROAD model it is hard to determine which approach is more accurate. There is, however, reason to be cautious in using PM estimates from the CARB model. There appear to be significant problems in the representation of TRUs in the OFFROAD database. For example, the NMOG values predicted from the emission factor derived in our TRU test multiplied by the fuel consumption from EMFAC yields a PM estimate that is 350 times smaller than the NMOG emissions that OFFROAD estimates. This is especially surprising since the TRU we tested was very old and had no emissions controls, whereas many of the TRUs in the fleet are much newer and cleaner, which would lead us to expect that the model's NMOG estimate would be lower than the number based on our emission factor, rather than 350 times higher.

PM estimated from the "PM production times fuel" is about 3.5 times smaller than the value obtained from the EMFAC and OFFROAD models' output (6.3 ton/day vs. 21.7 ton/day).

The majority of this discrepancy arises from the estimates of the three off-road categories. For example, the calculated 2-stroke primary PM emissions are 0.24 ton/day, whereas the modeled primary PM emissions are an order of magnitude higher (3.7 ton/day). The off-road diesel is the largest driver of the discrepancy on an absolute basis: the calculated and modeled values differ by 7.7 ton/day. This suggests that either (1) the actual fleet emissions of off-road diesels are much higher than the TRU emission factor that we used as a surrogate for all off-road diesel, (2) the ARB models are not accurate, or (3) some combination of these.

As already indicated from the apparent discrepancy in the TRU numbers, the second of these explanations seems very likely. Therefore it is difficult to make sweeping conclusions for the off-road sources. According to the "CARB primary PM" estimate and the "CARB primary PM+SOA" estimate off-road diesels are the dominant PM source. Indeed, the diesel off-road primary PM (9.4 tons/day) is almost as large as the sum of all the primary and secondary PM estimates in columns 8 and 9 of Table 5.1 (primary+SOA = 10.97 tons/day). Compared to the other CARB modeled emissions categories in column 10 of Table 5.1, it is roughly twice as large as the next closest source (uncontrolled HDDV at 5.29 tons/day).

Overall, this analysis suggests that SOA production can have a defining impact on net PM production when considered in the context of total fuel consumption in SoCAB by all the various combustion sources. The data indicate that on-road gasoline is currently significantly under-represented by EMFAC and OFFROAD models due to the large SOA contribution from this source. When SOA production is included in the analysis, newer LDGV become one of the largest sources of PM. In fact, if the three LDGV groups shown in Figure 5.5 are combined and SOA is included, LDGV are the largest PM source. This may overstate the importance of LDGV since off-road sources are expected to be a large PM source, but the contribution off-road sources remains highly uncertain, pending further experimental data. The on-road results, on the other hand, are expected to be very robust. This thesis shows that while on-road diesel vehicles are currently an important source of PM, LDGV are likely responsible for a larger fraction of ambient PM. This is a surprising result, but another recent study has come to the same conclusion using very different experimental methods [25]. It is anticipated that LDGV will become an even more important source once existing regulations requiring DPF retrofits on both on- and off-road sources are implemented over the next few years. Regulators are strongly urged to consider the impact of SOA on net PM production. We have clearly shown that for LDGV incorporating their SOA contribution is of first order importance.



Figure 5.4. Total gasoline and diesel consumption in 2010 for California's South Coast Air Basin (SoCAB) calculated using the California Air Resource Board's (CARB) EMFAC model for on-road sources and CARB's OFFROAD model for off-road sources (except commercial aircraft, marine vessels and locomotives). The three largest source subclasses for fuel consumption from five different source categories (2 on-road categories and 3 off-road categories) are indicated in the smaller series of satellite pie charts. On-road sources consume 92% of the fuel in SoCAB. LDV=light duty vehicle (passenger cars, SUVs and pick-up trucks weighing less than 5750 lb), TRU=transportation refrigeration unit (used to cool perishable cargo during transport), rec. equip=recreational equipment (e.g., snowmobiles, ATVs). Larger trucks are classified by weight: type 1 trucks (5751-14,000 lbs), type 2 trucks (14,001-33,000 lbs), type 3 trucks (>33,000 lbs). The sum of all the "other" categories in the figure is ~3% of the 23.4 million gallons of fuel used per day.



Figure 5.5. Net PM production in SoCAB in 2010 estimated by three different methods for three off-road sources and five on-road sources. The blue bars represent the PM mass predicted by the OFFROAD and EMFAC models for off-road and on-road sources, respectively. These values are also presented in Figure 5.3 and in column 10 of Table 5.1. The red bars represent the PM mass predicted by multiplying the primary PM production (from this research) and the fuel consumption from CARB models (result in column 8 of Table 5.1). The black bars represent the SOA mass (from this research) predicted by multiplying the SOA production and the fuel consumption from CARB models (result in column 9 of Table 5.1). The gold bars represent the sum of the blue bar and the black bar—the primary PM from CARB models plus the SOA derived from this research.

5.3 Policy Recommendations

Considerable progress has been made in mitigating air pollution in the United States in the last decade alone: nationally, PM2.5 concentrations are down ~25% since 2001. When considered in the light of the dramatic reduction in PM and other air pollutants already realized by the beginning of the 21st century in Los Angeles and other megacities in the U.S., there is cause for considerable optimism. However, much more remains to be done and, as has been demonstrated in this dissertation, there is considerable evidence for moving from our current

primary PM-centric approach to regulating PM emissions to one in which the crucial role of *secondary* organic aerosol is acknowledged. For example, there is little benefit still to be derived from further tightening primary PM emissions from light-duty gasoline vehicles (especially new vehicles), as they are already vanishingly small in comparison to the secondary emissions. Time and money would be better spent in California, for example, in supporting a campaign to identify important SOA precursors in LDGV emissions rather than in approving and enforcing the newly proposed 1-3 mg/mile LEV-3 PM standard. The SOA precursor problem may not be an easy one to solve. Our data show that with diesel fuel, for example, a simple reduction in aromatic content does not have any impact on SOA production. Nevertheless, a concerted effort by oil and car companies as well as government agencies similar to the reformulated gasoline studies undertaken in the 1990s would be expected to lead to much larger benefits than would regulations further tightening primary PM emissions.

A further recommendation with on-road vehicles is to investigate the amount of SOA produced from the oxidation of emissions from so-called super-emitters. These vehicles are known to have a disproportionately large impact on primary PM emissions, but nothing is known about their contribution to the SOA burden. Even for older vehicles which are not visibly smoking super-emitters it may be beneficial to consider retrofitting them with more effective oxidation catalysts because they are still probably emitting large amounts of SOA precursors.

Many more experiments are needed to characterize off-road emissions—primary as well as secondary. Off-road engines are expected to be a large source, but this dissertation only scratches the surface with respect to the amount of data necessary to characterize the SOA production from the vast range of sources in the off-road category. Furthermore, even the primary PM emissions in existing models (e.g., CARB's OFFROAD model) may be highly inaccurate, as our study of the diesel TRU indicate.

In both California and nationally, new non-road emission standards are expected to have a large impact on certain off-road primary emissions. However, the standards remain rather lax with respect to allowable NMOG. As some of these compounds are SOA precursors, the nonroad standard will not be as effective as it could be, and it is anticipated that off-road sources will continue to be responsible for significant amounts of SOA even after the new standards take effect.

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Chapter 6: Future Work

While there is an array of on-road gasoline vehicles with different emissions characteristics, the range of diversity is much smaller than with off-road combustion sources. Thus, it is difficult to accurately represent off-road sources with the relatively small sample size of engines tested in this work. Given the fact that off-road sources are driving much of the primary PM pollution, and many of these engines emit large amounts of NMOG, it is essential to test a wider range of SOREs and other off-road sources to better constrain their SOA contribution, and thus their net PM impact. In particular, we recommend further tests (and smog chamber tests) with TRUs including newer ones with aftertreatment devices such as DPFs. Our analysis indicates that construction and mining equipment are also potentially large contributors; therefore, it would be useful to characterize their SOA production.

We noted previously that SOA production during SORE chamber tests was sensitive to the VOC/NOx ratios. Our data were limited to measurements at a limited number of different ratios. Future work should include a careful characterization of the relationship between VOC/NOx ratios and SOA production for SOREs and possibly other combustion sources.

The analysis of emission factors and fuel consumption from a variety of sources described in the second part of the Synthesis and Conclusions could be expanded from SoCAB to a state and/or national level. Although we do not expect major differences in the conclusions, there are certain details of the vehicle and off-road fleets that are particular to southern California. For example, EIA data indicate that on a national basis medium and heavy duty trucks consume about one quarter of the fuel that light duty cars and trucks do [1]. In SoCAB, where personal vehicles are more frequently used (for getting everywhere in such a sprawling metropolis), medium- and heavy-duty trucks consume only about 10-13% as much fuel as cars. Such differences could shift certain conclusions made in this dissertation.

I continue to be amazed that there is not a single one-stop shop for succinct and up-todate information on emissions regulations. I have looked for such a compendium for the last 2 years of my graduate career and have still not found a comprehensive one for California or the U.S. There are a number of different sources that partially cover the regulatory landscape, but there is not to my knowledge any exhaustive reference. This would be an indispensable tool for those of us doing policy-relevant research. It should include information for all emission sources (gas, diesel, mobile, stationary, off-road, etc.), and it should be regularly maintained.

As discussed in chapter 3, DPF regeneration could lead to a small but non-negligible amount of SOA production. The work in this dissertation focused on stationary, forced regenerations, but it is unclear whether this is the most common or most important type of regeneration event. It is also not known how different the emissions from this type of regeneration are in comparison to a passive regeneration. We would speculate that passive regeneration is much more common, but it is not at all clear how and to what extent the emissions differ. From the larger perspective, SOA from regeneration is a very minor PM contributor at most, so this may not be a top research priority.

Only a few studies [2] have been published to date examining the toxicity of SOA, but this is an important area needing attention immediately. There is some evidence that the oxidized compounds in SOA could be more damaging to the body than elemental carbon, say, but the evidence in the literature is still rather thin. If it were determined (to oversimplify significantly), for example, that SOA is twice as toxic as EC or POA by some reasonable set of surrogate measurements, this weighting should be incorporated in assessing both the relative importance of particular sources and what aspects of those sources should be targeted (e.g., SOA precursors instead of particle traps).

Ultimately, the costs attending fuel reformulation, aftertreatment technologies or other PM mitigation schemes must be weighed against their net social benefit-the calculation of which depends on the spatially resolved predictions of ambient pollutant concentrations from chemical transport models (CTMs). In the future the SOA yields and PM emissions data described in this work should be incorporated into CTMs to simulate concentrations of fine PM and determine the relative importance of SOA to ambient PM levels. These tools could be used to predict PM mass and determine the SOA to POA split for baseline scenarios as well as possible future emission scenarios in which a variable percentage of vehicles are (1) switched to a different fuel (i.e., impact of large scale change to fuel chemistry) and/or (2) equipped with specific AT. These predictions could then become inputs to the U.S. EPA's BenMAP computer model-a tool which translates ambient concentrations into monetized health impacts. This model will allow policymakers to explore the benefits of introducing regulations aimed at limiting SOA, given varying characteristics (e.g., changing fuel chemistry or AT) of the U.S. motor vehicle fleet. It would also be useful to re-evaluate the EPA 812 cost-benefit of the Clean Air Act Amendments after incorporating the impact of SOA mitigation.

A number of studies have indicated the disproportionately large PM contribution of the class of vehicles referred to as super-emitters (cars emitting visible smoke) [3-5]. However, little is known about the SOA production from these vehicles' gas phase emissions. Presumably they emit a potent and high-yielding mix of SOA precursors, but I'm unaware of any smog chamber
studies characterizing them. Given the very large number of cars on the road, even if superemitters constitute only 1% of the fleet, they may be an important source of SOA precursors.

This thesis does not address evaporative emissions. Do they lead to significant SOA production? Evaporative emissions are currently modeled in EMFAC and OFFROAD, but little work has been done to quantify the SOA that may be produced from them.

We noted in the Synthesis and Conclusions that the OFFROAD model seems to overpredict emissions from the TRU category by several orders of magnitude. It may be important to perform a systematic validation of the source categories in the emissions models currently used.

In addition to the future work cited above, there are a number of near term projects that are directly connected to the current work that will be completed. The majority of these projects depend upon our receipt of the necessary data from the California Air Resources Board. Once we receive the speciated VOC data for the third field campaign the SOA yields of the most recently tested gasoline vehicles, which are currently estimated using an average emissions profile from the first field campaign, can be updated. In addition, instrument problems have prevented us from obtaining the IVOC data from the diesel vehicles and some of the gasoline vehicles. These will be updated soon. Once we obtain the speciated VOC data for the SORE chamber experiments we will also calculate the SOA yields for these experiments. For a number of the SORE chamber experiments NMOG data were not collected. For these experiments we will use a scaling factor based on the VOC/NOx to calculate the VOC consumed in the SOA production.

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