Considering the future of anthropogenic gas-phase organic compound emissions and the increasing influence of non-combustion sources on urban air quality

Peeyush Khare [1] and Drew R. Gentner [1, 2, *]

[1] Department of Chemical and Environmental Engineering, Yale University, New Haven CT-06511 USA

[2] School of Forestry and Environmental Studies, Yale University, New Haven CT-06511 USA

* To whom correspondence may be addressed. Email: drew.gentner@yale.edu

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Abstract

Decades of policy in developed regions has successfully reduced total anthropogenic emissions of gas-phase organic compounds, especially volatile organic compounds (VOCs), with an intentional, sustained focus on motor vehicles and other combustion-related sources. We examine potential secondary organic aerosol (SOA) and ozone formation in our case study megacity (Los Angeles), and demonstrate that non-combustion-related sources now contribute a major fraction of SOA and ozone precursors. Thus, they warrant greater attention beyond indoor environments to resolve large uncertainties in their emissions, oxidation chemistry, and outdoor air quality impacts in cities worldwide. We constrain the magnitude and chemical composition of emissions via several bottom-up approaches using: chemical analyses of products, emissions inventory assessments,

theoretical calculations of emission timescales, and a survey of consumer product material safety datasheets. We demonstrate that the chemical composition of emissions from consumer products, and commercial/industrial products, processes, and materials is diverse across and within product/material-types with a wide range of SOA and ozone formation potentials that rivals other prominent sources, such as motor vehicles. With emission timescales from minutes to years, emission rates and source profiles need to be included, updated, and/or validated in emissions inventories, with expected regional/national variability. In particular, intermediate-volatility and semivolatile organic compounds (IVOCs and SVOCs) are key precursors to SOA but are excluded or poorly represented in emissions inventories, and exempt from emissions targets. We present an expanded framework for classifying VOC, IVOC, and SVOC emissions from this diverse array of sources that emphasizes a lifecycle approach over longer timescales and three emission pathways that extend beyond the short-term evaporation of VOCs: (1) solvent evaporation, (2) solute off-gassing, and (3) volatilization of degradation by-products. Furthermore, we find that ambient SOA formed from these non-combustion-related emissions could be misattributed to fossil fuel combustion due to the isotopic signature of their petroleum-based feedstocks.

1. Introduction

Anthropogenic emissions of gas-phase organic compounds, including volatile organic compounds (VOCs), are of direct concern as toxic or carcinogenic air pollutants in indoor and outdoor environments (Cohen et al., 2005; Nazaroff and Weschler, 2004; Weschler and Nazaroff, 2008). Often they are more important for air quality as reactive precursors to the formation of outdoor tropospheric ozone and secondary organic aerosol (SOA) as well as indoor SOA, and thus play a central role in the elevated mortality and morbidity rates caused by fine mode particulate matter

(i.e. $PM_{2.5}$) and ozone in both developed and developing regions (Destaillats et al., 2006; Jerrett et al., 2009; Lim et al., 2012; Nazaroff and Weschler, 2004; Pope and Dockery, 2006; Sarwar et al., 2004; Singer et al., 2006; Weschler, 2011). In urban and downwind areas globally, 20-70% of $PM_{2.5}$ is organic aerosol (OA), with SOA comprising 58% of OA in urban areas and 82% downwind on average (Zhang et al., 2007).

Yields of SOA and ozone are strongly dependent on precursor molecular size, volatility, structure, and moieties/functionalities as well as environmental conditions (Gentner et al., 2012; Kroll and Seinfeld, 2008). SOA models have struggled to reproduce observations due to incomplete knowledge on SOA precursors and their sources (Hallquist et al., 2009; Kroll and Seinfeld, 2008). Gas-phase organic compound measurements and emissions data have historically focused on VOCs (i.e. C_2-C_{12} alkanes and VOCs with equivalent volatilities), but research has demonstrated the prevalence and importance of larger, intermediate-volatility and semivolatile organic compounds (IVOCs and SVOCs, respectively) (Gentner et al., 2012; Kroll and Seinfeld, 2008; Robinson et al., 2007; Zhao et al., 2014). With greater SOA mass yields, IVOCs and SVOCs are key for modeling and mitigating SOA but are less-studied due to measurement difficulties (Gentner et al., 2012; Goldstein and Galbally, 2007). While their emissions from motor vehicles have received more attention, emissions from most other sources are poorly constrained.

In recent history, motor vehicles, power plants, and residential combustion have been dominant drivers of detrimental air quality (e.g., VOCs, nitrogen oxides (NO_X), $PM_{2.5}$, ozone, sulfur dioxide (SO_2)), with automobiles dominating anthropogenic VOC emissions in major cities (Gentner et

al., 2017; Hao et al., 2007; McDonald et al., 2013, 2015; Warneke et al., 2012; Zhou et al., 2003). Yet due to the success of combustion-related emissions control policies over the past 60 years, motor vehicle VOC (and other pollutant) emission factors have decreased by orders of magnitude in route to today's diesel and gasoline vehicles, albeit with some recent on-road diesel NO_X compliance issues (Hao et al., 2007; Kirchstetter et al., 1999; U.S. Environmental Protection Agency, 2011; Warneke et al., 2012). In no other place has this been more studied than Los Angeles, CA, where $PM_{2.5}$ and ozone still exceed standards, and OA comprises 41% of PM_1, 66% of which is SOA (Hayes et al., 2013; Warneke et al., 2012). Recent work has suggested that motor vehicle emissions in L.A. cannot fully explain observations of reactive precursors and SOA (Ensberg et al., 2014; Hayes et al., 2015; McDonald et al., 2015; Zhao et al., 2014). In L.A. and beyond, the role of motor vehicles in degrading air quality will decline further with the newest on-road emissions standards (e.g. Tier 3/LEV-III, Euro 6/VI) (Figure 1), use of electric-powered vehicles, and stricter regulations on emissions from off-road vehicles and other engines (Gentner et al., 2017; Giannouli et al., 2011; Gordon et al., 2013; Platt et al., 2014; Tessum et al., 2014; Weiss et al., 2011).

The main objective of this paper is to evaluate anthropogenic sources of gas-phase organic compounds that are gaining prominence as motor vehicles and other combustion-related sources become cleaner in the developed and developing world. We demonstrate that consumer products and commercial/industrial products, processes, and materials are important, widely-distributed area sources of VOCs, IVOCs, and SVOCs with variable source profiles making their emissions and impacts difficult to observe and constrain. Our demonstration builds on relevant indoor air quality studies observing emissions and substantial SOA formation from ozone-initiated reactions

with emissions from consumer products, building materials, and cleaning products (Chang et al., 2011; Destaillats et al., 2006; Gold et al., 1978; Lewis, 2001; Mitro et al., 2016; Nazaroff and Weschler, 2004; Singer et al., 2006; Weschler, 2011; Weschler and Nazaroff, 2008; Wilke et al., 2004) as well as secondary emissions from oxidative degeneration of indoor paints, varnishes, and materials (Knudsen et al., 1999; Poppendieck et al., 2007a, 2007b; Salthammer and Fuhrmann, 2007).

We outline a holistic framework to assist future research in the field, and then use a multi-dataset approach to constrain emissions, which includes the most detailed emissions inventory available, laboratory analysis of product composition, a survey of consumer product material safety datasheets (MSDSs), and calculations of emissions timescales from theory. Specifically, we (a) evaluate the pathways, chemical composition, and magnitude of VOC, IVOC, and SVOC emissions from prominent types of products, processes, and materials; (b) calculate their potential to form SOA and ozone; and (c) compare their emissions and potential air quality impacts to other prominent sources**.** We identify major knowledge gaps in emission rates and composition, including I/SVOCs, which we explore via two examples: pesticides and asphalt-related emissions.

2. Defining a comprehensive framework for non-combustion-related emissions

There is a wide body of work on some aspects of emissions from products, processes, and materials in indoor or outdoor environments, but outdoor-focused emissions inventories are mostly focused on evaporative emissions of VOC solvents at the time of application. Here we outline the current

111 scope of emissions and expand on it to define a comprehensive framework to guide future studies
112 on this class of emissions.

113

114 ***Volatility:*** Emissions of gas-phase organic compounds can and should be differentiated by their
115 volatility: VOCs, IVOCs, and SVOCs, or further by their n-alkane-equivalent volatility (Murphy
116 et al., 2014). One can broadly refer to compounds emitted from products and processes as
117 products/process-related emissions.

118

119 ***Source categories:*** While the spectrum of sources is very diverse, they are often grouped by use.
120 The following source categories are consistent with the most detailed VOC inventories for
121 consumer products, but are extended (shown with * below) to incorporate a broader array of
122 materials and products, including those used in commercial and industrial processes:

123 - Paints (indoor and outdoor),
124 - Industrial adhesives,
125 - Consumer adhesives,
126 - Sealants,
127 - Pesticides (consumer and agricultural),
128 - General cleaning products,
129 - Targeted cleaners,
130 - Personal products (e.g. beauty and hygiene),
131 - Building materials (e.g. carpeting, flooring, insulation, wood, gypsum),*
132 - Furnishings (e.g. furniture),*

- Paving and roofing asphalt-related materials,
- Solid consumer products and packaging (e.g. plastics, elastomers), and their additives (e.g. plasticizers, flame retardants).*

However, the volatility range of most of the existing categories needs to be expanded to completely include I/SVOCs. We discuss I/SVOC-containing pesticides and asphalt-related products/processes as examples that are not sufficiently included in inventories (see Section 4.1.3). Notes: we exclude gasoline evaporation (from vehicles or fuel stations) and fossil fuel extraction/processing given their close connection to combustion. We briefly discuss food-derived cooking emissions for comparison, which are important and classified separately.

Emission pathways: We propose three general pathways of product/process-related emissions:

1) Evaporation of solvent from a product while it is in storage or being used, or during a process;
2) Volatilization of solute or active compounds from an applied coating or a solid product/material (i.e. off-gassing); and
3) Volatilization of by-products from the degradation or transformation of solute or active compounds, or a solid product/material.

The first is the principal pathway previously considered and often occurs over faster timescales (minutes-days) from liquids like cleaners, paints, and other solvents. The second acts over longer timescales (weeks-years), is not always included in inventories, and is a key potential source of I/SVOCs (see Section 4.1.3). SVOC pesticides, flame retardants, and off-gassing plastics are examples studied for indoor air quality (Batterman et al., 2009; Brodzik et al., 2014; Clausen et

al., 2004; Faber et al., 2013; Kemmlein et al., 2003; Lewis, 2001; Wensing et al., 2005; Weschler and Nazaroff, 2008). The third is due to the generation of degradation by-products via thermal or photochemical stress, exposure to oxidants (i.e. OH, O_3, or NO_3), or other reactive chemical processes. These may have longer emission timescales depending on oxidant concentrations and the chemical and physical properties of degradation precursors. These emissions are largely understudied with the exception of asphalt-related emissions and ozonation of indoor materials (Poppendieck et al., 2007a, 2007b; Salthammer and Fuhrmann, 2007; Toftum et al., 2008).

A lifecycle approach: Emissions during application or immediate use are most commonly studied, but many emissions related to products, process, and materials occur over much longer timescales. In the future, emissions studies need to include all three potential emissions pathways across full lifecycles of:

- Storage,
- Transport,
- Application,
- Curing,
- Active use,
- Weathering,
- Restoration,
- Removal and disposal.

There are too many facets within the lifecycles of each source category to discuss in this paper, but our case study on asphalt-related emissions in Section 4.1.3 demonstrates several aspects.

Production methods are not explicitly included here since they may fall under the purview of industrial point sources, but with small, distributed production it may be appropriate to consider the industrial/commercial processes as area-wide sources. Chemical transformations of materials or products across their lifetimes need to be considered since they can influence the chemical composition and rates of emissions. For example, transformations can occur during a wide variety of in-use conditions or during the storage of unused or partially-used products/materials, both of which can be over long storage periods in a variety of environmental conditions. Application methodology is a determining factor in both emission rates and composition during application. For example, common methods include direct liquid application or aerosolization, either via a pressurized can or a nozzle and air compressor, and aerosolization provides a direct emission pathway for all components and subsequent evaporation of aerosol droplets. Finally, emissions in latter parts of lifecycles (i.e. weathering/deterioration, restoration, removal, and disposal) all need to be considered.

3. Methods

We constrain the magnitude, chemical composition, and potential air quality impacts of emissions using multiple bottom-up approaches: chemical characterization of a selection of consumer products via gas chromatography-mass spectrometry and carbon isotope mass spectrometry; a detailed assessment of emissions inventories and estimation of source contributions to potential SOA and ozone formation; theoretical calculations of emission timescales; and a survey of reported chemical composition in consumer product MSDSs. Details on the emission timescale calculations can be found in Appendix B, and other additional

methods details pertaining to potential SOA and ozone estimation can be found in the supporting information.

Chemical speciation of consumer products: We selected 17 consumer products across a range of product types with attention to those with unresolved alkane or aromatic mixtures (Table 1). Top-selling products from major commercial providers were selected in order to make a realistic assessment of products that are currently in significant public use, and to avoid biasing the analysis towards less-common products. With a limited sample size, only 1 water- and 1 ethanol-based product were included. Diluted samples were prepared at a concentration of 1000 ng μL^{-1} in either hexane or toluene depending upon the product composition provided in their MSDS. The chemical composition of the emittable fraction of products was determined using gas chromatography with electron ionization-mass spectrometry (GC-EI-MS) (Agilent 7890B/5977). A 1µL syringe (Hamilton) was used to directly inject the sample onto the GC column through an inlet held at 320 ºC. During each injection, the column was initially held at 40 ºC for 2 minutes, then ramped at 10 ºC min^{-1} to 325 ºC and lastly held at 325 ºC for 5 minutes. Mass spectra of background subtracted individual ion peaks were used to identify compounds in a sample using the NIST mass spectra library. Calibration curves were drawn for five different concentrations of authentic standards (AccuStandard) for diesel range alkanes (C_{10}-C_{28}), purgeable aromatics, and terpenes. The emittable organic fraction of raw products is defined by volatility and approximated as VOCs + IVOCs via our chemical analysis and reported MSDS data (Note: SVOCs excluded in this analysis to focus on compounds that are fully partitioned to the gas-phase at equilibrium under typical conditions). A carbon isotopic analysis was also carried out at the Keck Carbon Cycle Accelerator Mass Spectrometer (AMS) facility at U.C. Irvine to measure carbon-14 (‰ $\Delta^{14}C$) and carbon-13

(‰ $d^{13}C$) relative to carbon-12 via a 0.5MV Compact AMS (National Electrostatics Corp.), and estimate the fossil carbon content in individual products.

Urban emissions inventories: We used the California Air Resources Board (CARB) Almanac emissions inventory and the U.S. EPA SPECIATE 4.4 source profiles to generate the total and compound-specific emissions for California and Los Angeles (Cox et al., 2013; U.S. Environmental Protection Agency, 2014). The CARB emissions inventory is the most detailed available with respect to source categories and basin-level rates. Los Angeles is our case study megacity given its historical role in air quality research and policy with a multi-decadal record of emissions data, ambient measurements, field campaigns, and publications (Bishop and Stedman, 2008; Fortin et al., 2005; Neligan, 1962; Warneke et al., 2012). In addition, the U.S. National Emissions Inventory and emission inventories from the Global Emissions Initiative (GEIA) were used for nationwide and worldwide comparison of VOC emissions respectively from solvents and on-road motor vehicles.

We estimated total daily potential ozone and SOA formation in greater Los Angeles from the product/process-related emissions included in the CARB inventory. Values were also calculated for exhaust and evaporative emissions from on-road motor vehicles using CARB's Emission Factors (EMFAC) model database and literature ozone and SOA yields for each source pathway and low-emission vehicles (LEV) generation (Gentner et al., 2013, 2017; Zhao et al., 2017). Potential ozone formation values are based on maximum ozone incremental reactivity (MOIR) values from the SAPRC-07 inventory (Carter, 2007; Gentner et al., 2013). The very diverse range

of compound classes used in products, materials, and processes remain largely understudied with respect to their SOA yields (e.g. esters, siloxanes). Hence, specific literature SOA yields were used wherever possible (Algrim and Ziemann, 2016; Chacon-Madrid et al., 2010; Chan et al., 2010; Gentner et al., 2012; Kwok and Atkinson, 1995; Ng et al., 2006; Pankow and Asher, 2008; Sadezky et al., 2006; Tsimpidi et al., 2010), and estimated for other unstudied compounds without existing SOA yields (see Table S6 for details). SOA yields are estimated at 10 µg OA m^{-3} in urban, "high-NO_X" conditions (approx. >5 ppb). Ozone and SOA yields for each analyzed consumer product and product categories are compared to other key sources. The SOA yields provide a conservative, lower estimate of potential SOA without aqueous SOA despite studies showing that aqueous pathways to SOA increase SOA yields for small oxidized precursors or their oxidation by-products (Daumit et al., 2016; Jia and Xu, 2014). For the case study city Los Angeles (and Mexico City), aqueous SOA formation was relatively small during major field studies (Dzepina et al., 2009; Hayes et al., 2015; Washenfelder et al., 2011). However, future work in other cities should consider aqueous SOA given the magnitude of oxygenated fraction in product/process-related emissions (see section 4.1.2).

Survey of material safety datasheets (MSDS): We obtained the MSDS data by surveying a set of 88 MSDS entries from the websites of major home improvement stores focusing on their top-selling products. Five product categories were chosen including paints, adhesives, cleaning products, sealants and pesticides. Chemical composition information was extracted from the "composition/information on ingredients" section reported in the datasheets. MSDS entries for commercial products frequently report 30% to 60% of product composition as "proprietary

mixtures", so this survey only identifies the presence and establishes general ranges for current product types (Table 2).

4. Results and Discussion

4.1 Composition and magnitude of product/process-related emissions

The organic composition of consumer products and commercial/industrial products, materials, and processes are very diverse, which leads to similar diversity in emissions, and further region/nation-specific heterogeneity can be expected. We calculate the magnitude and average chemical composition of emissions from source categories included in the CARB emissions inventory and SPECIATE database (Figure 2a) with the goal of assessing the distribution of emissions across organic compound classes and product types (i.e. source profiles) in a megacity with the most representative inventory available. We find that the consumer products and commercial/industrial processes that comprise product/process-related sources are large emitters of a diverse suite of VOCs, but view these results as a lower estimate given likely missing emissions, such as those discussed in Sections 2 and 4.1.3.

4.1.1 Chemical composition

Laboratory analysis of consumer products: Our results summarized in Table 1 demonstrate the prevalence of non-benzene, single-ring aromatics and C_6-C_{12} alkane mixtures as solvents, and the presence of IVOCs and SVOCs in consumer products. The emittable fraction of products ranged from 3-100%, and the single-ring aromatic and IVOC content ranged from 3.5-93% and 0.77-95%,

respectively. Another key result of this analysis is the frequency of many functionalized aliphatic or aromatic VOCs and IVOCs that are not traditionally measured in atmospheric monitoring (e.g. esters, acetates, siloxanes), which is echoed in the MSDS survey results. More detailed speciation results with a breakdown of alkanes and single-ring aromatic compounds can be found in Table S1. Validation of real-world product/process-related emission rates/timescales is necessary to advance the field but will require examining a wide range of products and geographic conditions.

Analysis of emissions inventories: Figure 3(a) shows the estimated overall composition of product/process-related emissions in Los Angeles averaged over the years 2005 to 2020 determined by combining SPECIATE source profiles with the CARB emissions inventory for the South Coast Air Basin (SoCAB). Alcohols and miscellaneous emissions together make up 50% of the total product/process-related emissions with ethanol as one of the largest individual species emitted, which is consistent with SoCAB ethanol observations that were substantially greater than what would be expected with gasoline vehicles as the only source (Gouw et al., 2012). 70% of the miscellaneous emissions are made up of mineral spirits whose composition varies greatly with application but are generally comprised of acyclic and cyclic $C_{7\text{-}12}$ alkanes with variable amounts of aromatic content. The remaining 30% includes unresolved asphalt mixtures, oxygenates, fragrances, and undefined petroleum distillates/oils/spirits, some of which also fall into the I/SVOC category discussed below. Single-ring aromatics are estimated at 13% of total emissions with a mix of 43% toluene, 38% C_8, 3% C_9, and 1.5% C_{10} aromatics, and minor PAH emissions. Carbonyls represent 10% of total emissions, 36% of which is acetone. Anthropogenic terpenoid emissions in the inventory, while highly reactive, are small relative to other sources and biogenic contributions (see section S.4 in SI).

Figure 3(b) shows the distribution of organics in the SoCAB emissions inventory from major product/process-related source categories. Paints emerged as the highest VOC emitter, ~21% of which is single-ring aromatics (Figures 3(b) and S4). Targeted cleaners, pesticides, and general cleaners were the next largest source types in the inventory. A more detailed breakdown of emissions broken up by source category and compound class can be found in Table S3. We used the EPA SPECIATE database for source profiles in this study, which had a national scope, some inclusion of I/SVOCs, and greater chemical detail (i.e. number of species). We examined changes in the chemical speciation of total emissions with CARB's 2010 adjustment to SPECIATE in the final years of our study period. We found minor differences in the overall emissions (Figure S5) that are largely attributable to changes in the assignment of unspeciated (i.e. miscellaneous) VOC and I/SVOC emissions that do not affect our conclusions. Differences in potential SOA and ozone in the SoCAB for 2010-2020 (Section 4.2) are not clear due to uncertainties in these changes to unspeciated assignments, and the uncertainties in SOA yields.

MSDS survey: Summarized in Table 2, the greatest single-ring aromatic content was observed in adhesives (8%) and sealants (9%), while the 30 surveyed paints did not have aromatic VOC content in contrast to the SPECIATE source profiles (Figures 3(b) and S4). In comparison, the chemical speciation of 42 major products categorized as 'solvents' (across C_{6-13}) in 2002 reports a wide range of total aromatic content (0-100%) and an average of 41% (±46%) with the remainder comprised of acyclic and cyclic alkanes (Censullo et al., 2002). Differences when compared to our present-day laboratory and MSDS paint speciation show reductions in aromatic content due to increasingly stringent regulations in the U.S. However, for other locations, it highlights the likely,

continued prevalence of single-ring aromatics in solvents, especially for developing regions. We also found that MSDSs did not report I/SVOCs content in the composition of pesticides. However, we observed 8%-95% IVOC content in the emittable fraction of the pesticides samples analyzed in our laboratory. For all of the product categories examined, and especially for pesticides, the amount of compositional information provided by the MSDSs is limited and hinders our ability to constrain the average aromatic or I/SVOC content since compounds outside the VOC range are often not disclosed due to proprietary claims or regulatory exemptions, and where provided all compound concentrations are usually provided as a wide range. For example, under "fragrance exemptions" VOCs and IVOCs are often not disclosed and can even be labeled as "VOC-free".

4.1.2 Emission rates

While motor vehicles are still major sources in developed regions, their total gas-phase organic compound emissions have been gradually declining with the continued implementation of stricter emissions standards (Gentner et al., 2017), increasing the relative importance of other sources (Figures 1, 2a). At a global scale, the MACCity and ACCMIP emissions inventories estimate global solvent-related VOC emissions of 15 Tg yr^{-1} in 2000 and year-over-year increases since 1960 (speciated by aromatics, C_{6+} alkanes, ketones, alcohols, and other VOCs), and emissions of aromatics from solvents are expected to outweigh those from transportation in 2020 (7.5 vs. 6.7 Tg yr^{-1}) (GEIA, 2017). The 2014 U.S. National Emissions Inventory (NEI) data reports that VOC emissions from solvent-related sources are just 25% less (300 tons day^{-1}) than those from on-road mobile sources nationally, while they exceed on-road emissions by 25% (21 tons day^{-1}) in California (U.S. Environmental Protection Agency, 2011). Figure S1 shows California's statewide bi-decadal emissions estimates from CARB where product/process-related VOCs will reach 450

356 tons day^{-1} in 2020, exceeding motor vehicles by 116 tons day^{-1}. A similar picture may emerge in
357 developing nations, as the control of motor vehicle emissions is greatly accelerated by the
358 advancements and knowledge of developed nations; such that emission standards in major
359 emerging economies employ either U.S. or E.U. policies, and are generally only one generation
360 behind (Kodjak, 2015). International studies over the past 2 decades show highly varying
361 contributions (~5-45%) to the total anthropogenic VOC emissions from just "solvent" use at both
362 regional and national scales (summarized in SI) (van den Born et al., 1991; Caserini et al., 2004;
363 Chen et al., 2009; Deguillaume et al., 2008; Lu et al., 2007; Markakis et al., 2009; Menut, 2003;
364 Nielsen et al., 2008; Piccot et al., 1992; Song et al., 2007; U.S. Environmental Protection Agency
365 and Office of Air Quality Planning and Standards, 1991).

366

367 Emissions inventory data for Los Angeles demonstrate that anthropogenic emissions have
368 consistently decreased over the last four decades (Figure 2a), which is consistent with ambient
369 observations (1960-2010) (Warneke et al., 2012). As the contribution of on-road motor vehicles
370 to total anthropogenic emissions has declined, product/process-related sources have become a
371 major contributor of VOCs. Based on the CARB emissions inventory, contributions of
372 product/process-related sources are the largest single contributor of VOC emissions in the basin
373 and state (Figures 2a & S1), and are growing with population (i.e. increased in-basin usage). While
374 consumption volume is low compared to combustion fuels, emission factors are higher given that
375 most of the volatile components are emitted whereas fuels are burnt at ≥ 99% efficiency. Yet, no
376 region can be fully representative of product/process-related emissions on a larger scale, and
377 regional/national specifics will influence the magnitude and composition of emissions. For

example, California's extensive regulations will modify the composition of products sold in CA, and likely elsewhere in the U.S.

4.1.3 Emissions of intermediate- and semi-volatile organic compounds (IVOCs and SVOCs)

Despite representing only a small to moderate amount of emissions, IVOCs and SVOCs from motor vehicles are key precursors to urban SOA (Gentner et al., 2012; Robinson et al., 2007). Similarly, we conclude that consumer products and commercial/industrial processes are also large sources of unspeciated IVOCs and SVOCs, some of which are included in the CARB inventory, while there is evidence that some other source pathways are not.

Many common products/materials (e.g. pesticides, fragrances, foams, plastics) have IVOCs or SVOCs that partition to reach equilibrium and evaporate over long timescales (Figure 4) (Batterman et al., 2009; Clausen et al., 2004; Mitro et al., 2016; Weschler and Nazaroff, 2010). Our chemical analysis revealed IVOCs or SVOCs in 10 of the 17 products (Tables 1 & S1). Including the MSDS survey, we found composition ranging from 0% to 95% I/SVOCs, with I/SVOCs present in 23% of cleaners, 20% of adhesives, 24% of paints, and 46% of sealants (Table 2). Aliphatic or aromatic I/SVOCs are frequently used in some types of pesticides and are sometimes replaced with biogenic oils (e.g. neem oil, fish oil), such that the bulk of the pesticides in our MSDS survey were comprised of < 1 - 10% active compounds and a balance of undisclosed, "non-hazardous" ingredients.

399 The SPECIATE profiles and CARB emissions inventory include some estimates of unspeciated
400 "low-vapor pressure VOCs (LVP-VOCs)" in consumer products that are defined as larger than 12
401 carbon atoms (or equivalent volatility), which is roughly consistent with the beginning of the IVOC
402 range (California Air Resources Board, 2015b). While poorly constrained, non-aromatic I/SVOCs
403 included in the inventory constitute ~3% (6 tons day^{-1}) of total SoCAB emissions estimates in the
404 CARB/SPECIATE case study, 90% of which is classified as unspeciated "LVP-VOCs". Consumer
405 product pesticides, general purpose cleaners, and targeted cleaners (e.g. laundry) are the largest
406 sources of I/SVOC contributions emitting 3.6, 1.0 and 0.4 tons day^{-1} of I/SVOCs, respectively.
407 Consumer product pesticide emissions had the highest fraction of I/SVOCs (29%).

408

409 While CARB's consumer products inventory includes I/SVOCs due to manufacturer reporting
410 requirements, I/SVOCs are exempt from limits on VOC content except for multipurpose solvents
411 and paint thinners, and there are known limitations in their coverage, especially of oxygenated
412 species (California Air Resources Board, 2000, 2015b). We conclude there are other anthropogenic
413 sources of IVOCs and SVOCs that have not been considered due to their long emission timescales
414 (i.e. days-years; Figure 4, Table S9) (de Gouw et al., 2011; Weschler and Nazaroff, 2008). We
415 present evidence for two such examples in this paper: I/SVOC-containing pesticides and asphalt-
416 related products, materials, and processes, but other examples include the volatilization of I/SVOC
417 solvents, solutes, or solids (e.g. coatings, flame retardants) and materials that may degrade to form
418 compounds with volatilities of $C_{13\text{-}26}$ n-alkanes (e.g. construction materials/coatings, including
419 materials with petroleum distillates/residues, mineral oil, coal tar, or similar).

420

Example 1: Emissions of IVOCs and SVOCs from pesticides: We have several pieces of evidence that demonstrate pesticides (including herbicides, insecticides, and fungicides) contain I/SVOCs, but they also highlight the fact they are poorly documented and regulated. We analyzed the chemical composition of three pesticides available as consumer products and they were comprised of 8%, 20% and 95%, IVOCs in the $C_{14\text{-}17}$ range (Table 1, Figure S3), with trace levels of larger compounds. Our MSDS survey (Table 2) was inconclusive for pesticides since the majority of consumer pesticides are not disclosed in MSDSs due to claims of proprietary mixtures, non-regulated components outside of the VOC range, and/or because they use naturally-derived oils (e.g. neem oil). Studies have shown such naturally-derived oils are comprised of aliphatic and aromatic I/SVOC-range compounds (Isman, 2000; Kumar and Parmar, 19996). Our emissions inventory analysis shows that non-aromatic I/SVOCs are the largest inventoried source of I/SVOCs (Figure 3), but the lack of data in MSDSs and VOC exemptions from regulations suggest this is a lower estimate of actual emissions. To examine commercial/industrial products, we also analyzed the composition of three petroleum-based pesticides used in agriculture (Figure S2), which are comprised of C_{16}-C_{26} cyclic and acyclic alkanes mostly in the SVOC range that are applied as thin films via a sprayed water emulsion. These can partition to the gas phase and be re-emitted on the timescales in Figure 4 and may impact urban (or downwind) areas in agricultural regions, with 18-29 Gg applied yr^{-1} in California. California-wide emissions from applied agricultural pesticides were nearly one-fifth of that from consumer products in 2015. However, the high I/SVOCs fraction in their composition and potential to emit over long timescales makes them an important consideration for air quality.

Example 2: Emissions of IVOCs and SVOCs from asphalt-related products, materials, and processes: We propose asphalt-related products/processes as important sources of IVOCs and SVOCs whose emissions are currently underestimated in inventories and require better quantification. Asphalt-containing materials are used in road paving and repair (and similar applications for roofing or other surfaces), and are comprised of petroleum-derived organic compounds; predominantly non-distillable (i.e. non-volatile) asphalts sometimes with smaller amounts of VOCs, IVOCs, and/or SVOCs. They are used as sealers, coatings, and binders; mixed with aggregates to pave roads; and applied using either high application temperatures, water emulsions, and/or solvent.

The three paving/roofing-related products we analyzed contained aliphatic and aromatic VOCs and IVOCs up to C_{18} present as solvents, with minor SVOC content (Figure S3). Similarly, there were no I/SVOCs declared in the asphalt-containing products in our MSDS survey. Non-solvent emissions during the hot storage, application, or resurfacing of these asphalts are caused by the degradation (i.e. fragmentation) of larger organic compounds from asphalts to form smaller compounds (C_7-C_{30}), which include cyclic and acyclic alkanes, single-ring aromatics, PAHs (2-, 3-, and 4-ring), and sulfur- or nitrogen-containing species (i.e. benzo- and dibenzo- thiophenes and furans), all of which were not present in the asphalt prior to heating (Cavallari et al., 2012b; Gasthauer et al., 2008; Kitto et al., 1997; Kriech et al., 2002; Lange et al., 2005; Lange and Stroup-Gardiner, 2007; The Asphalt Institute & European Bitumen Association, 2015). The total mass and composition of emissions is dependent on production methods, asphalt grade, and increases in magnitude and maximum molecular weight with storage/application temperatures (i.e. more SVOCs at high temperatures), which ranged 100-240 ºC, or higher for roofing asphalts (Cavallari

et al., 2012c; Gasthauer et al., 2008; Kitto et al., 1997; Kriech et al., 2002; Lange et al., 2005; Lange and Stroup-Gardiner, 2007; The Asphalt Institute & European Bitumen Association, 2015).

Emissions of aromatic and aliphatic VOCs, IVOCs, and SVOCs from heated asphalt mixtures ("hot mix") during application have also been documented in occupational health studies on "asphalt fumes" (Cavallari et al., 2012a, 2012b; Kriech et al., 2002; Lange et al., 2005; Lange and Stroup-Gardiner, 2007). Yet, current emissions inventories do not include emissions of VOCs, IVOCs, and SVOCs from the degradation of larger compounds during and after the application of asphalt mixes. Estimation methods focus solely on the evaporation of VOC solvents from "cutback asphalt", which is a mixture of asphalt and solvent, included as an area source in the "solvent evaporation" category in Californian, U.S., and E.U. inventories (California Air Resources Board and Sonoma Technology Inc., 2003; European Environment Agency, 2017; San Joaquin Valley Air Pollution Control District, 2008; U.S. Environmental Protection Agency, 2014; U.S. EPA, 1995). Road paving solvents are prohibited in non-attainment areas in California (Table S4), so emissions in the SoCAB case study are minor (1 ton day^{-1}) and mostly smaller than C_{10} in the SPECIATE source profiles (Table S5) (Cox et al., 2013).

Emission factors of degradation byproducts don't exist, so we approximate lower limits on emission factors only for the period immediately during application using limited published data (see section S.3 in SI), but longer timescale experiments are necessary. Calculated lower limits range from 100-2000 mg kg^{-1} of asphalt (not including aggregate) with a strong dependence on application/storage temperature. This is on the same order as motor vehicle emission factors and

488 is greater than CARB's current emission factor for hot-mix asphalt (District, 2012; Gentner et al.,
489 2017; San Joaquin Valley Air Pollution Control District, 2008). Yet, California's asphalt
490 consumption of 1,540,000 tons liquid asphalt year^{-1} (Table S4) represents statewide I/SVOC
491 (+VOC) emissions of 0.5 – 8 tons day^{-1} during application alone (The Asphalt Institute, 2015).
492 This does not overwhelm current solvent-VOC emissions from paving/roofing (33 tons day^{-1}) but
493 emphasizes the need for further research since the poorly-constrained emissions largely include
494 I/SVOCs emitted over long timescales which are known to have high SOA yields.

495

496 Asphalt-related emissions exemplify the stated need for lifecycle-focused approaches, with
497 potential emissions across storage, transport, application, curing, weathering (e.g. degradation due
498 to climate or UV radiation), and resurfacing. Their magnitude and composition will vary with
499 production/handling methods, geologic source, and application type and location (esp. climate).
500 Emission pathways (from Section 2) include (1) volatilization of application solvents and (3) the
501 production and release of degradation byproducts while (2) does not apply due to negligible off-
502 gassing from extremely low volatile un-degraded asphalt constituents. The emission of asphalt
503 degradation products may peak during construction-related activities primarily due to asphalt's
504 exposure to high temperatures during its storage, application, or resurfacing. Still, seasonal highs
505 in surface temperature (summer pavement maximums are 47-67 ^{o}C and up to 70 ^{o}C for roofs
506 (Parker et al., 1997; Pomerantz et al., 2000)), will likely affect the rate of internal transport and
507 diffusion out of the "cured" asphalt layer resulting in emissions extended over its lifetime. (Note:
508 paving solvents are currently assumed to be emitted over several months (California Air Resources
509 Board and Sonoma Technology Inc., 2003)).

510

4.2 Potential SOA and ozone formation of product/process-related emissions compared to other major sources

Products and processes emit a diverse array of organic compounds (Figure 3). Some are of relatively-low direct concern for human health (e.g. terpenoids), while others present issues as primary emissions, especially in indoor or concentrated workplace environments (e.g. aromatics, ethers, PAHs). Yet, most are reactive and will oxidize in outdoor or indoor environments to form oxidized VOCs with unknown, but large potential health effects (Pöschl and Shiraiwa, 2015). This section focuses on their impacts on air quality via SOA or ozone formation. However, the health or environmental effects of the primary emissions should be especially considered in developing regions where primary VOC emissions are larger, or for specific compound classes near sensitive natural environments. A comparison of the SOA yields and ozone formation potentials for major source categories (Figure 5) demonstrates that product/process-related emissions have SOA yields and ozone formation potentials that are on par with other major urban sources such as motor vehicles and are strongly dependent on composition.

SOA formation potential: The potential SOA from on-road gasoline vehicles in greater Los Angeles region has decreased by ~65% between the years 1990 and 2015. By 2020, further reduction by 25% is expected relative to the 2015 value of 3.3 tons day^{-1}. These numbers for diesel vehicles are 75% and 1.3 tons day^{-1}, respectively. If the emissions inventory is accurate, then the 2015 potential products/process-related-SOA in the SoCAB basin is nearly equal to the SOA formation potential of on-road gasoline and diesel vehicles, and is estimated to surpass them by 2020 with an increasing share of SoCAB's total anthropogenic emissions (Figure 2b). While single-ring aromatics and PAHs constitute only 11% of the total product/process-related

emissions, they are responsible for ~80% of the potential SOA from those sources in the region (4% PAHs and 76% single-ring aromatics, largely toluene and xylenes). Existing emission inventories badly underestimate emissions of I/SVOCs and their contributions to SOA. They are shown to be responsible for 0.18% of products/process-related-SOA, but this excludes 87% of the total I/SVOCs emissions which are labeled as unspeciated "LVP-VOCs" in the inventory and thus have no assigned SOA yield in calculations. Additionally, our calculations do not include "missing" emissions or their potential SOA. Anthropogenic terpenoids, including lemon oil, pine oil, orange oil, orange terpenes, D-limonene and α-pinene, are responsible for ~8% of the total product/process-related SOA.

It is important for future work to consider modifying factors for SOA (and ozone) formation chemistry. Relative VOC to NO_X ratios have been shown to affect the chemistry and production rates of SOA and ozone (Hallquist et al., 2009; Sillman, 1999; Zhao et al., 2017). For many cities outside Los Angeles, urban air quality develops within a backdrop of biogenic emissions of VOCs and IVOCs, which is critical to keep in mind as we pursue stricter emission targets for reactive organics. In some cases, such as in the Southeast U.S., biogenic emissions dominate over anthropogenic gas-phase organics, and emissions of SO_2 and NOx are large drivers of biogenic SOA formation (Xu et al., 2015). Similarly, gas-phase cooking emissions from food represent an additional uncertain source in urban air quality along with cooking POA which has been more studied (Bruns et al., 2017; Hayes et al., 2013; Klein et al., 2016).

555 ***Ozone formation potential:*** Over the past several decades, potential ozone has been dominated by
556 emissions from gasoline motor vehicles. Yet, in 2015 potential ozone from gasoline vehicles was
557 only 30% greater than product/process-related sources, and by 2020 product/process-related
558 emissions will surpass on-road motor vehicle contributions in the basin (Figure 2c). Potential
559 ozone from on-road diesel vehicles in 2015 is only ~5% of that from product/process-related
560 sources. Contributions to potential ozone from product/process-related sources are 33% alcohols,
561 29% aromatics, and 12% alkanes (not including unspeciated "LVP-VOCs") (Table S2). A recent
562 ozone formation sensitivity analysis of solvent-related emissions speciation with 22 lumped
563 species demonstrated that using input source profiles that are more detailed in terms of contributing
564 compound classes would improve ozone model performance (von Schneidemesser et al., 2016).

565

566 ***Contributions from off-road combustion-related sources:*** Off-road mobile sources are also
567 significant sources of reactive precursors to SOA and ozone across a very diverse mix of sources
568 and fuels (Cox et al., 2013; Gordon et al., 2013; May et al., 2014; Zhao et al., 2016). These sources
569 have received greater regulatory attention in the past 20 years, and control policies (e.g. CARB,
570 EPA) will add additional variance to the magnitude and composition of emissions (California Air
571 Resources Board, 2017; Miller and Facanha, 2014; U.S. EPA, 2017). Given the limited
572 information on their diverse source profiles, and thus their SOA and ozone yields (Gordon et al.,
573 2013; McDonald et al., 2015), we constrain their uncertain contributions independent from on-
574 road sources. Their fraction of VOC emissions in the SoCAB leveled off and started to decrease
575 after 2005 (Figure 2a), and in 2015 the ratio of on- to off-road emissions in the ARB inventory is
576 1.5:1 and 1:2 for gasoline- and diesel-powered engines, respectively, when including equipment,
577 recreational vehicles, boats, trains, and aircraft that use either gasoline or diesel (Cox et al., 2013).

Given similar ozone and SOA yields to on-road gasoline or diesel vehicles, off-road emissions could approximately increase potential SOA and ozone from gasoline- and diesel-related sources by 67% and 200%, respectively, in 2015 (SoCAB). Yet, this is subject to the uncertainty from the wide range of engines, fuels, and emission controls affecting the composition of emissions. These results are generally consistent with the relative source contributions of on- and off-road sources to total OA reported by McDonald et al. (2015) for 2010. The current outsize impact of off-road sources, despite using a relatively small amount of fuels, is due to the fact that emission factors are much higher, such as 2+ orders of magnitude higher for gasoline off-road compared to on-road sources (Gordon et al., 2013; McDonald et al., 2015; Zhao et al., 2016). The inclusion of off-road sources does not affect our conclusion that non-combustion sources and motor vehicles (on- and off-road) contribute similar amounts of potential SOA and ozone in our case study megacity around the 2015-2020 period, especially with a rapidly growing role for non-combustion sources as combustion emissions are further controlled. In all, this highlights the importance of continued assessment and regulation of off-road combustion-related sources as part of a holistic air quality management plan.

4.3 Empirical ambient evidence for IVOC and SVOC emissions, and their SOA contributions

Ambient measurements (2010) of I/SVOCs in our case study city are consistent with our findings; they demonstrate that IVOCs are important contributors to SOA in the region and other urban areas, but major uncertainties persist regarding the sources of primary IVOC emissions (Hayes et al., 2015; Ma et al., 2016; Zhao et al., 2014). Recent model results estimate that 70-86% of urban

SOA in Pasadena come from the oxidation of primary I/SVOC emissions (Ma et al., 2016). Zhao et al. (2014) state that unidentified non-vehicular sources contribute 'substantially' to these emissions but no clear fraction is yet established. A major fraction of SOA cannot be explained without the inclusion of IVOCs or other unspeciated organics (Gentner et al., 2012, 2017; Hayes et al., 2015; Jathar et al., 2014; Zhao et al., 2014). Other results indicate that fossil-related sources contribute approximately half of OA and a majority of fresh, urban SOA in Los Angeles (Gentner et al., 2017; Hayes et al., 2013; Zotter et al., 2014). Yet, bottom-up estimates and top-down assessments of the SOA produced from gasoline and diesel vehicles (on- and off-road) cannot explain all of the observed fossil SOA in LA in 2010, which supports our conclusions and suggests the presence other major sources of fossil-derived SOA precursors (Ensberg et al., 2014; Gentner et al., 2017; Ma et al., 2016; McDonald et al., 2015; Zhao et al., 2014).

4.4 Isotopic carbon content and interpreting ambient isotopic data

The isotopic carbon content (i.e. ^{14}C vs. ^{13}C vs. ^{12}C) of organic aerosol has been used directly, and in tandem with source apportionment of bulk aerosol data from an aerosol mass spectrometer, to infer fossil vs. non-fossil origin of carbonaceous aerosols and their SOA precursors at several locations (Ceburnis et al., 2011; Hayes et al., 2013; Zotter et al., 2014). We tested the potential effect of products/process-related emissions on the interpretation of isotopic measurements of ambient SOA, and our isotopic analysis of 12 products demonstrates that their VOC and I/SVOC emissions and thus SOA will be depleted in Carbon-14 (Table 1). 8 of the 12 contained 97% or more fossil carbon, while the remaining 4 contained 57-81% fossil carbon. Asphalt-related sealants, solvents (e.g. paint thinner, naphtha), and pesticides were found to have the highest fossil carbon content. This is consistent with the fact that petrochemical feedstocks derived from

623 petroleum and other fossil fuels are used in the products, materials, and processes discussed
624 throughout this work.

625

626 Studies in greater Los Angeles (Pasadena) report that fossil-fuel driven emissions appear to
627 contribute 68%-74% of the observed afternoon increase in SOA formed from urban sources with
628 the remaining ~25% coming from non-fossil sources, principally regional biogenic and local
629 cooking sources (Hayes et al., 2013, 2015; Zotter et al., 2014). The observed fossil SOA and its
630 potential precursor sources have been analyzed across several studies with differing conclusions
631 (Bahreini et al., 2012; Gentner et al., 2017; Hayes et al., 2013; Zotter et al., 2014). The studies
632 agree that on-road diesel vehicles are a relatively minor contributor to fossil SOA (Bahreini et al.,
633 2012; Hayes et al., 2013, 2015; Zotter et al., 2014), and along with other papers, have proposed
634 the importance of other, unconstrained anthropogenic sources (e.g. off-road sources). (Ensberg et
635 al., 2014; McDonald et al., 2015; Zhao et al., 2014). Other evidence suggests a fossil source other
636 than on-road diesel since concentrations of IVOCs show only minor weekday vs. weekend
637 variation with changes in diesel traffic (Zhao et al., 2014). Based on our results and the evidence
638 in the literature, we conclude that fossil-derived urban SOA precursors are emitted from
639 product/process-related sources, and are responsible for some of the fossil SOA observed in the
640 SoCAB. The isotopic signature of products, materials, and processes is due to their petrochemical
641 feedstocks, and this has led to their misattribution to combustion-related sources in the past.

642

643 **5. Conclusions and future research needs**

644 Using multiple bottom-up approaches, we demonstrate the growing importance of non-combustion
645 emissions of gas-phase organic compounds from anthropogenic sources. Yet, our understanding
646 has been inhibited due to the chemical diversity of emissions across a myriad of source types, their
647 fossil isotopic signatures, and in many cases their prolonged emission timescales, which occur
648 over full lifecycles and a broader range of emissions pathways than is typically considered.
649 Emission timescales can extend over months or longer (Figure 4) in the case of sources of
650 I/SVOCs, emissions via transport through thick layers of materials/coatings or the formation and
651 emission of degradation by-products. The implications of these prolonged timescales are a legacy
652 of unreleased potential emissions built up or "banked" in the products and materials spread across
653 urban areas.

654

655 It is critical to emphasize that these results do not justify deviating attention from, or relaxing
656 emission standards for, combustion-related sources since they are still prominent factors in urban
657 air quality in the developed and developing world, and remain dominant contributors of carbon
658 dioxide. For the foreseeable future in many locations, they remain principal contributors of reactive
659 organic precursors and other criteria pollutants, especially in near-source hotspots, such as
660 roadways. Rather, we conclude that in order to support the coming decades of policy, modern air
661 quality research needs to holistically consider the full portfolio of anthropogenic (and biogenic)
662 sources that impact urban air quality. We highlight key research needs to support this objective.

663

664 ***A broad perspective on non-traditional sources of reactive carbon:*** This analysis highlights the
665 importance and further consideration of VOC, IVOC, and SVOC sources that have not received

sufficient attention to effectively support policy. With the successful control of "low-hanging fruit" where single source types dominated emissions, the control of a broader array of disparate sources becomes necessary. It is likely that there are other non-vehicular sources of reactive gas-phase organics in urban areas (e.g. food-derived cooking emissions), which need to be better included in inventories and models. Monitoring, studies, and inventories need to comprehensively include functionalized compound classes rather than just traditional classes.

Validation of existing emissions inventories: Our results based on exiting emissions inventories are subject to uncertainties in their methodology. Given the results, further research is needed to review, evaluate, and validate both the emissions factors and source profiles in emissions inventories. A lifecycle approach should include lifetime emissions over the three pathways stated in Section 2 which include solvent evaporation, solute volatilization and emissions via formation of degradation by-products. Such emissions will be seasonally-dependent on factors such as air velocity, relative humidity, and temperature (Wolkoff, 1998). A large survey of products and materials with attention to national/regional differences is warranted to ensure that source profiles accurately represent product/process-related emissions, including "green"-intentioned options for comparison. Single-ring aromatics are a key example; the current CARB inventory using the SPECIATE source profiles reports large emissions of single-ring aromatics, 72% of which comes from paints. Yet, this is in contrast to our MSDS analysis of prevalent products, which observed little aromatic content in the surveyed U.S. paints (Table 2).

Inclusion of IVOCs and SVOCs in emissions inventories: There is a clear need for more detailed emissions inventories of I/SVOCs from all sources. Further research should support the evaluation of the I/SVOC exemption in strategic air quality management plans, and composition reporting requirements in MSDSs and similar databases. More detailed chemical speciation with newer methods is required to accurately determine the SOA (and ozone) formation potential of unresolved I/SVOC mixtures. In the process, attention should be paid to heterogeneity in products containing petroleum distillates and similar components, which are very broad and can result in an equally broad range of emissions.

The off-gassing of I/SVOCs (and VOCs) from materials was not experimentally tested in this study and is not included in inventories. Recent studies have shown plastics, foams, and building materials off-gas I/SVOCs and VOCs (e.g. aromatics, aliphatics, halocarbons, terpenes, organophosphates, and oxygenated species) (Brodzik et al., 2014; Faber et al., 2013; Kemmlein et al., 2003; Toftum et al., 2008; Wensing et al., 2005). Similarly, detailed lab and field characterization of asphalt-related emissions over long timescales is needed to constrain emission factors, source profiles, and the effect of modified asphalts.

Understanding the application method and environment is key to determining air emissions of I/SVOCs since some products may be used with water and disposed of into wastewater, described as *down-the-drain factors*. For example, a recent ozone modeling study modeled the fate of 23 oxygenated I/SVOCs (e.g. glycols, glycol ethers, esters, alcohols) present in cleaning and personal products that are used with water. They concluded that most of the compounds that go down-the-

drain do not volatize and are biodegraded at wastewater treatment plants, while >90% of compounds that volatize outdoors will react with OH and contribute to ozone formation (Shin et al., 2015).

Quantifying outdoor transport of indoor emissions: Similar to *down-the-drain* factors, we highlight the need for a similar factor to determine fractions of indoor emissions that are permanently lost to indoor sinks via chemical or physical deposition (*fraction lost to indoor sinks*). Similarly, models will need factors to account for the increase in characteristic emission timescales when products/materials used on indoor surfaces remain indoors longer due to generally lower vertical transport coefficients and subsequent re-partitioning to other surfaces prior to transport outdoors.

Inter-location variability in the developed and developing world: While we present annual trends for our case study megacity Los Angeles, a similar situation is evolving elsewhere in developed urban areas where emissions of anthropogenic organics are key drivers of SOA and ozone formation, especially in megacities. We expect substantial heterogeneity between locations in the composition of emissions from products, materials, and processes due to national/regional regulations governing formulation, as well as climate, application specifics, and consumer preferences and options. In particular for this work, California's advanced regulatory program may have led to the phase out of some components in U.S. products. So globally the composition and magnitude of product/process-related emissions may contain a much greater fraction of reactive species, such as single-ring aromatics. Top-down ambient studies and bottom-up studies for other

731 locations are needed to confirm the importance of product/process-related emissions, and air
732 quality modeling studies should support these efforts. The situation in urban areas of developing
733 regions and emerging economies is uncertain since they have motor vehicle emissions
734 standards/technologies that may be much more advanced than the rest of their air quality
735 management plans (Kodjak, 2015). In such locations, non-combustion sources may be important
736 sources, but the combustion of fossil fuels or biomass for home heating/cooking and agricultural
737 waste disposal will play a larger role than in developed regions. In all locations, the magnitude of
738 regional biogenic emissions and SO_2/NO_X emissions will affect the impact of anthropogenic
739 organics on SOA.

740

741 ***Understudied oxidation pathways and products:*** The oxidation pathways and products for many
742 of the functionalized compound classes discussed in this work (e.g. Figure 3) are largely
743 understudied, with a lack of experimental or theoretical studies to constrain the generation of
744 SOA, ozone, and oxidized gases. Such oxidation products/pathways are also particularly
745 important in indoor environments, so research on their precursor emissions and subsequent
746 oxidation is also important for indoor air chemistry.

747

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Supporting Information. Please see the supplemental material for additional details on relevant regulations, methods, Tables S1-S9, and Figures S1-S5.

Appendix A: Current and historical regulations and policy on non-combustion products and processes

Emissions from consumer products and industrial processes received some attention in pre-2000 outdoor air quality research and policy, especially in the cases of toxic components, highly-reactive volatile solvents that fueled rapid ozone production (e.g. alkenes), and stratospheric ozone-depleting chemicals. Emissions of a select few hazardous air pollutants (HAPs) (e.g. benzene and vinyl chloride) were first broadly regulated under the U.S. Clean Air Act (1970). Subsequent amendments through 1990 required the U.S. Environmental Protection Agency (EPA) to regulate key sources of precursors to ozone production and emissions of 189 newly-designated HAPs (now "air toxics"), some of which were used in products and processes (National Research Council, 2004). Less well-known, the 1990 amendments also required the EPA to identify priorities and guidelines to mitigate emissions from consumer and commercial products (National Research Council, 2004). Several categories of paints and solvents were subsequently identified based on results from paint drying and chamber experiment studies conducted during early 1970s through late 1990s (Chang et al., 1997; Clausen et al., 1990, 1991, 1993; Hansen, 1974; Sparks et al., 1999; Sullivan, 1975), and regulations were established for half of the product categories, but actions were ultimately halted as these sources were not viewed as central to ozone or other criteria

776 pollutant mitigation at the time (National Research Council, 2004). Despite large uncertainties
777 about emissions and ambient contributions from products/processes, this strategy reflects the
778 magnitude and impact of motor vehicle emissions in 1990 (Figures 1-2); the keen focus on ozone
779 production; and the lack of knowledge on SOA formation chemistry and I/SVOCs.

780

781 U.S. state or air basin-level regulations vary with region and attainment status. California's air
782 quality policy and regulations have been the most inclusive and detailed with respect to emissions
783 from consumer products and some industrial processes. The California Air Resources Board
784 (CARB) started the Consumer Products Regulatory Program in 1991, and a similar Coatings
785 Program, to address outdoor and indoor air quality problems associated with their emissions by
786 placing product type-specific limits on VOC content, and total reactivity limits (i.e. ozone
787 potential) specifically for aerosol coatings (California Air Resources Board, 2015b). CARB is also
788 required to maintain statewide and county/basin-level emissions inventories for 72 source
789 categories, available 1975 to 2020. Within these categories, the product/process-related sources
790 include consumer products, architectural coatings, pesticides, cleaning and surface coatings, and
791 asphalt paving/roofing. Chemically-speciated emissions profiles for sources within these
792 categories are in the US EPA's SPECIATE repository, some of which are used by the European
793 Union (EU) (Pernigotti et al., 2016). In the 2015 California code of regulations report, CARB has
794 further updated regulations focusing on VOC emissions from antiperspirants and deodorants,
795 hairsprays, other consumer products (both aerosol and non-aerosol), and aerosol coating products
796 (California Air Resources Board, 2015a).

797

798 The Economic Commission of Europe employs market-based mechanisms to reduce regional
799 emissions of VOCs. The National Emissions Ceilings directive sets country-specific reduction
800 targets on organic gas emissions ranging from 10% up to 60% from 2010 to 2020 (European
801 Environment Agency, 2010). The EU has two relevant policy directives: the 'VOC Solvents
802 Emissions Directive' to limit industrial VOC emissions resulting from processes such as printing,
803 surface cleaning, vehicular coating, and dry cleaning; and the 'Paints Directive' to reduce VOC
804 content in paints and varnishes (European Commission, 2014). In China, in addition to restrictions
805 on criteria pollutants including both PM_{10} and $PM_{2.5}$, the Chinese Air Pollution Control Action
806 Plan 2013 also limits VOC emissions from paints, adhesives and petrochemical industry, and
807 promotes the use of low-volatility water-based paints (Ministry of Environmental Protection,
808 2012).

809

810 **Appendix B: Calculating characteristic timescales for emissions from surface layers**

811 The timescale for emission is defined by the simple relation:

812 $$\tau_{emission} = \frac{M_{applied}}{R_{emission}} \quad (1)$$

813 The mass applied ($M_{applied}$) and rate of emission ($R_{emission}$) are defined as in Weschler and
814 Nazaroff (2008), as a function of emission velocity (v_e) refers to the airborne mass transfer from
815 the surface of the applied layer to the free-stream air, which is the rate-limiting step compared to
816 diffusion within the thin layer (Weschler and Nazaroff, 2008). The gas-phase saturation
817 concentration immediately above the surface (C_{sat}) is determined by molecular structure, C_O is the
818 concentration of a compound in the layer, A is the exposed surface, and d is the depth of the layer.

819 $$R_{emission} = v_e A C_{sat} \quad (2)$$

$$M_{applied} = C_O A d \quad (3)$$

Plugging in Eqns. 2-3 into Eqn. 1, and substituting in the partitioning coefficient between octanol and air (K_{OA}), one gets Eqns. 4 and 6: Octanol is chosen as the proxy for the mixed organic layer that is applied. K_{OA} is available for a wide range of species and is consistent with previous modeling of SVOC partitioning from surfaces (Weschler and Nazaroff, 2008).

$$\tau_{emission} = \frac{C_O A d}{v_e \mathrm{A} C_{sat}} = \frac{C_O d}{v_e C_{sat}} \quad (4)$$

$$\text{since: } K_{OA} = \frac{C_o}{C_{sat}} \quad (5)$$

$$\tau_{emission} = \frac{K_{OA} d}{v_e} \quad (6)$$

v_e is a function of aerodynamic and boundary layer resistances ($r_a \; and \; r_b$), and can vary dramatically across indoor and outdoor environments. Given the diversity of compositions, applications, and environments that products and materials will be applied, constraining v_e is uncertain and highly variable. Calculations in Table S9 and Figure 4 are shown for a range of v_e from 10 m hr^{-1} to 50 m hr^{-1}, which covers a mix of moderately stable to neutral meteorological conditions. Higher values regularly occur for transport from in/out of some plant canopies. Urban values are strongly dependent on the urban landscape and regional meteorology; vertical transport velocities in built up urban areas like Paris range 5-20 m hr^{-1} (Cherin et al., 2015). Indoor values can decrease to < 5 m hr^{-1} due to lower friction velocities, which is still fast enough to for the emissions and chemistry that drive indoor air quality (Weschler and Nazaroff, 2008). 10 - 50 m hr^{-1} was chosen as a daytime range, but we acknowledge that slower vertical velocities and thus longer persistence on surfaces (i.e. lifetimes) may exist for some locations, especially indoors.

Equations 7-11 to calculate v_e, r_a, and r_b are reproduced below for location/condition-specific analyses.

$$v_e = \frac{1}{r_a + r_b} \quad (7)$$

$$r_a = \frac{1}{\kappa u^*} \ln\left(\frac{z_r}{z_0}\right) \quad (8)$$

$$r_b = \frac{5Sc^{2/3}}{u^*} \quad (9)$$

$$Sc = \nu/\mathcal{D} \quad (10)$$

$$u^* = \kappa U_r \left[\ln\left(\frac{z_r}{z_0}\right)\right]^{-1} \quad (11)$$

where u*: friction velocity, z_0: roughness length, z_r: reference height, U_r: reference velocity, κ: von Karman constant, Sc: Schmidt number, ν: kinematic viscosity, $\mathcal{D}$: gas diffusivity. Depending on the relative impact of r_a vs. r_b, decreases in diffusivity with larger molecules may affect transport.

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Figure captions

Figure 1. Characteristic evolution and modernization of in-use motor vehicle fleets. Trends in motor vehicle population, fuel use, and VOC emissions for model years conforming to pre-LEV, LEV-I, -II, and -III emissions standards in California's South Coast air basin for 1990-2020 from CARB's EMFAC database (California Air Resources Board, 2014).

Figure 2. Emissions and potential air quality impacts of product/process-related sources and motor vehicles over time in the South Coast air basin (i.e. Los Angeles). (a) Total VOC emissions (excluding ethane). (b) Potential SOA from product/process-related emissions compared to on-road motor vehicles, with uncertainties based on the ranges of compound class-specific SOA yields, and (c) Ozone formation potential via compound-specific maximum ozone incremental reactivity values (SAPRC, no uncertainty given). Product/process-related results are produced using CARB emissions data and EPA source profiles; see methods for further detail. Note: None of the panels include VOCs, IVOCs, or SVOCs, from products/processes that we identify in Sections 2 and 4 as missing from emissions inventories, but SOA and ozone formation from motor vehicle emissions does include I/SVOCs. Maximum potential SOA from gasoline vehicles in 1990 was ~41 tons day^{-1} (off graph). Pre-1990 potential SOA and ozone for motor vehicles is excluded due to the lack of fleet-resolved data.

Figure 3. Average emissions from product/process-related sources for 2005-2020 based on data from CARB inventory and SPECIATE database as a function of (a) compound class (shown with standard deviations) and (b) major product/process-related source categories in the inventory (values in Table S3). "Miscellaneous" contains 70% mineral spirits ($C_{7\text{-}12}$ hydrocarbons). I/SVOCs does not include an estimate of the missing emissions identified in Section 2 and 4.

Figure 4. Emission timescales for single-ring aromatics, alkanes, and prominent solvents: ethanol (a), ethylene glycol (b), and acetone (c). Based on applied layers of 0.01-1 mm and vertical transport coefficients for neutral/stable outdoor conditions (10-50 m hr^{-1}), with longer timescales in indoor environments or thicker layers

(e.g. asphalt, building materials). The left axis is reproduced on the right in days. Timescales are limited by gas-phase transport from the surface, but absorption into polymeric or porous substrates could extend timescales (Weschler and Nazaroff, 2008). Volatility range boundaries for VOC-IVOC and IVOC-SVOC occur between C_{12}-C_{13} and C_{19}-C_{20}, respectively, for n-alkanes or compounds with equivalent volatilities. See Appendix B for calculations and Table S9.

Figure 5. Comparison of (a) SOA yields and (b) Ozone formation potential of five major sources. Blue markers represent average yields of the product/process-related source categories in Figure 3, and do not include "missing" emissions. The red markers show yields of sampled consumer products calculated from speciation obtained after GC-MS analysis. All are shown as a function of mass emitted, not product composition.

FIGURES & TABLES

Table 1. Composition and emittable fraction of twelve commercially available consumer products, and results of their carbon isotope analysis. Please see Table S1 for detailed mass distribution profiles and Table S7 for detailed carbon isotopic analysis results.

Product name	Percent Fossil Origin	IVOC Content	Aromatic Content	Emittable Fraction	$d^{13}C$ (‰)	$\Delta^{14}C$ (‰)
Naphtha cleaner	>99%	-	-	100%	-29.0 ± 0.1	-999.4 ± 0.5
Non-polar solvent	>99%	-	93%	100%	-27.4 ± 0.1	-998.5 ± 0.5
Fogging Insecticide[†]	>99%	95%	-	95%	-26.7 ± 0.1	-999.1 ± 0.5
Semi-gloss furniture coating	56%	-	6%	30%	-29.9 ± 0.1	-565.4 ± 0.7
Multipurpose solvent[a]	>99%	-	-	100%	-30.6 ± 0.1	-997.8 ± 0.7
Furniture coating[†]	65%	-	1%	40%	-30.2 ± 0.1	-650.0 ± 0.6
Roof paint[b]	>98%	-	-	-	-22.7± 0.1	-985.0 ± 0.5
Sealant[c, §]	97%	0.77%	21%	25%	-27.4 ± 0.1	-969.9 ± 0.5
Paint thinner[†]	>99%	2%	3%	100%	-29.1 ± 0.1	-999.7 ± 0.5
Asphalt coating[d, §]	>99%	4%	3%	25%	-27.6 ± 0.1	-994.8 ± 0.6
Detergent[e]	81%	3.5%	4%	25%	-27.9 ± 0.1	-807.8 ± 0.6
General purpose cleaner[f, †]	81%	1%	-	3%	-27.7 ± 0.1	-811.1 ± 1.3
Multipurpose lubricant	-	39%	-	97%	-	-
Aerosol Coating Product[g, †]	-	-	12%	17%	-	-
Flashing cement[h, §]	-	0.2%	3.5%	27%	-	-
Crawling Insecticide 1[i, †]	-	20%	-	20%	-	-
Crawling Insecticide 2[j, †]	-	8%	-	8%	-	-

*Crude oil and plant-derived ethanol were used for multiple reference blanks (Table S8).
[§]Asphalt-related products.
[†]Applied as aerosols.
[a] Largely consists of acetone (80%) with the rest as cyclotetrasiloxanes and aryl halides.
[b] Water based product. Other components include titanium dioxide, silica and aluminum hydroxide.
[c] Largely consists of petroleum asphalt, clays and cellulose.
[d] Largely consists of petroleum asphalt.
[e] 46% of the emittable fraction (EF) consists of mostly esters, 70% of which have less than 12 carbon atoms. Terpenes including limonene, eucalyptol and α-terpineol form 37% of the EF.
[f] Water-based product. Also has terpenes including camphene, d3-carene, α-pinene, linalool and δ-limonene. 60% of terpene fraction is δ -limonene.
[g] Contains 35% acetone and 25% hydrocarbon propellants not included in the EF. *25% of EF is 75% acetate + 25% ketones.
[h] Largely consists of petroleum asphalt, kaolin, cellulose and aluminum magnesium silicate.
[i] Contains 15% hydrocarbon propellants not included in the EF.
[j] Contains 25% hydrocarbon propellants not include in the EF.
Note: All fractions given in the footnotes refer to the emittable fraction of a product. Emittable fraction is confirmed with MSDS where possible.

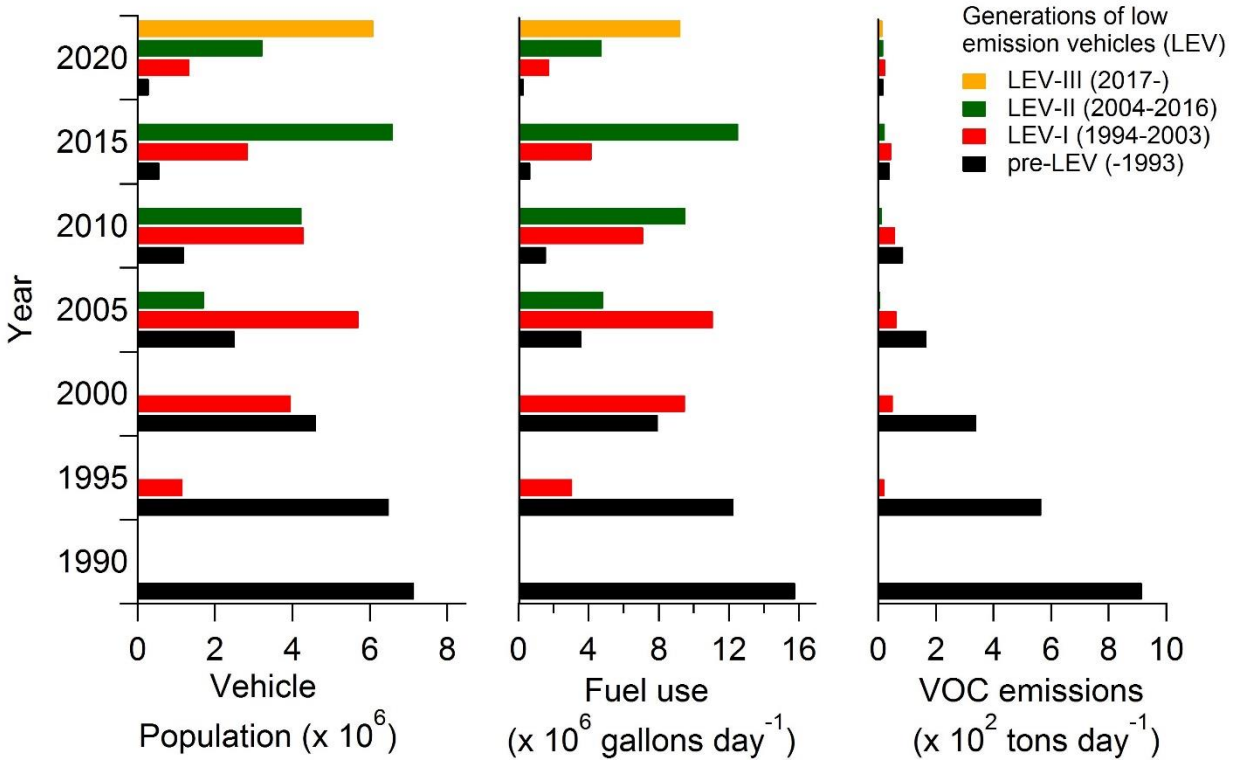
1384 **Table 2.** Analysis of material safety data sheets commercially available with products.

1385

Product Category	Fraction of products with aromatic content	MSDS Aromatics %wt. Mean (range)	Fraction of products with I/SVOC content	MSDS I/SVOCs %wt. Mean (range)
Paints*	0%	0	24%[a]	2.5 (1-5)
Adhesives	27%	8 (1-30)	7%[b]	20 (10-30)
Cleaning Products	8%	5 (1-10)	23%[c]	3.5 (1-7)
Sealants	53%	9 (1-30)	7%[d]	4 (1-10)
Pesticides**	NS	NS	NS	NS

[a]Consists of benzoates. Log K_{OA}=7.75 which puts them in the IVOCs range.
[b]Does not include potential emissions from petroleum asphalt which on average constitutes 36% in 13% of the surveyed products. 50% products contain 38% limestone on average.
[c]Includes C9-C14 ethoxylated alcohols.
[d]Does not include potential emissions from petroleum asphalt which on average constitutes 40% in 33% of the surveyed products. 60% products contain 36% limestone on average.
*20% of MSDSs include 'non-hazardous' or 'proprietary' component in composition ranging from 60%-100%.
**MSDSs do not present sufficient information on the composition of pesticides (NS: not sufficient).

1386



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1389 **Figure 1.** Characteristic evolution and modernization of in-use motor vehicle fleets. Trends in motor vehicle

1390 population, fuel use, and VOC emissions for model years conforming to pre-LEV, LEV-I, -II, and -III emissions

1391 standards in California's South Coast air basin for 1990-2020 from CARB's EMFAC database (California Air

1392 Resources Board, 2014).

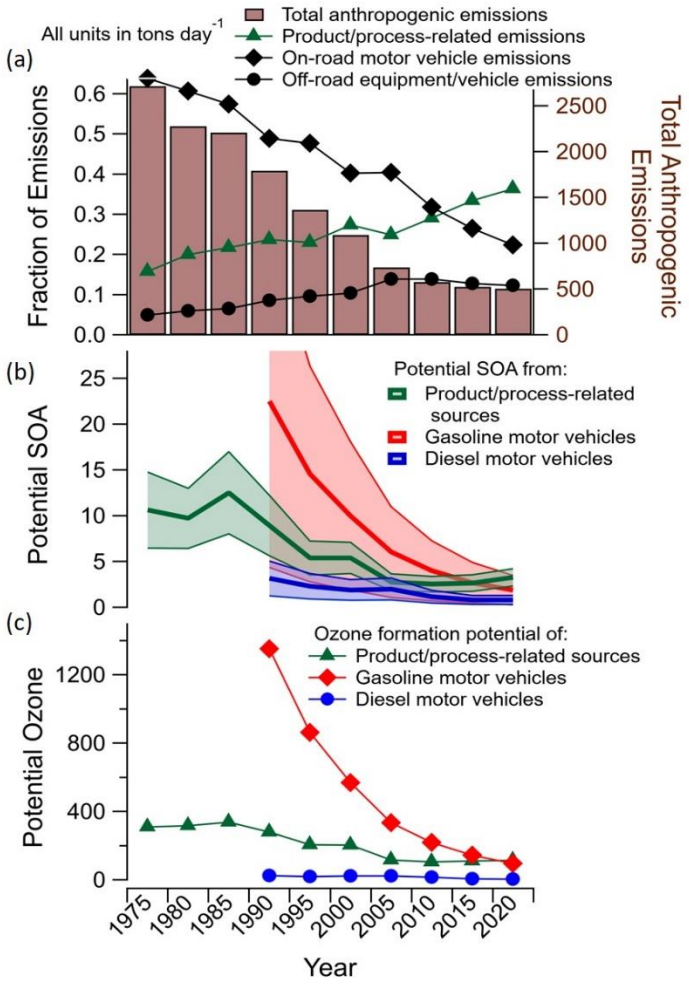


Figure 2. Emissions and potential air quality impacts of product/process-related sources and motor vehicles over time in the South Coast air basin (i.e. Los Angeles). (a) Total VOC emissions (excluding ethane). (b) Potential SOA from product/process-related emissions compared to on-road motor vehicles, with uncertainties based on the ranges of compound class-specific SOA yields, and (c) Ozone formation potential via compound-specific maximum ozone incremental reactivity values (SAPRC, no uncertainty given). Product/process-related results are produced using CARB emissions data and EPA source profiles; see methods for further detail. Note: None of the panels include VOCs, IVOCs, or SVOCs, from products/processes that we identify in Sections 2 and 4 as missing from emissions inventories, but SOA and ozone formation from motor vehicle emissions does include I/SVOCs. Maximum potential SOA from gasoline vehicles in 1990 was ~41 tons day^{-1} (off graph). Pre-1990 potential SOA and ozone for motor vehicles is excluded due to the lack of fleet-resolved data.

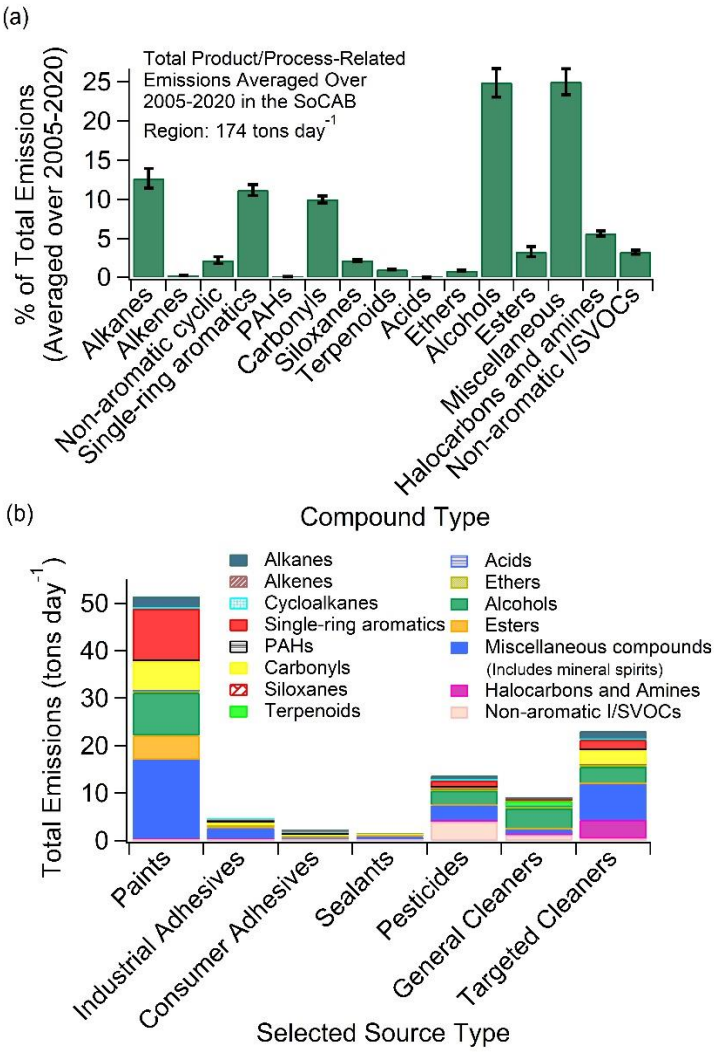
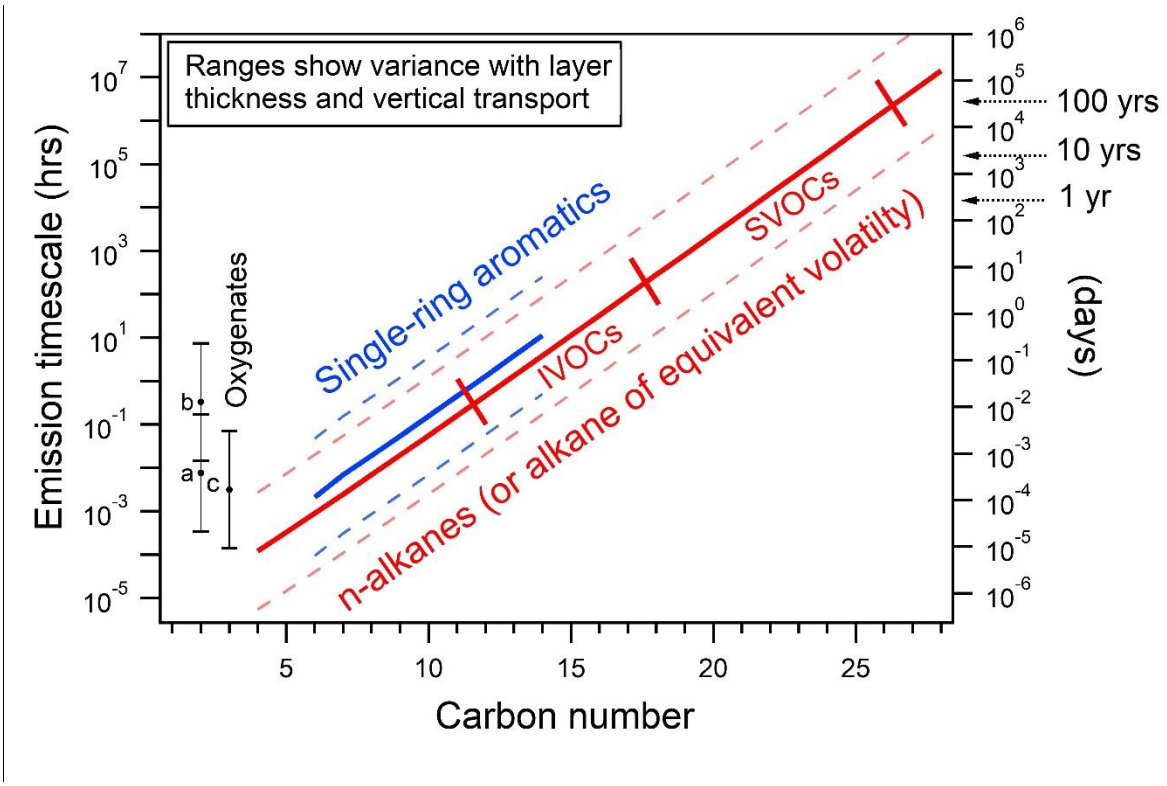


Figure 3. Average emissions from product/process-related sources for 2005-2020 based on data from CARB inventory and SPECIATE database as a function of (a) compound class (shown with standard deviations) and (b) major product/process-related source categories in the inventory (values in Table S3). "Miscellaneous" contains 70% mineral spirits (C_{7-12} hydrocarbons). I/SVOCs does not include an estimate of the missing emissions identified in Section 2 and 4.



1412

1413 **Figure 4.** Emission timescales for single-ring aromatics, alkanes, and prominent solvents: ethanol (a), ethylene
1414 glycol (b), and acetone (c). Based on applied layers of 0.01-1 mm and vertical transport coefficients for
1415 neutral/stable outdoor conditions (10-50 m hr^{-1}), with longer timescales in indoor environments or thicker layers
1416 (e.g. asphalt, building materials). The left axis is reproduced on the right in days. Timescales are limited by gas-
1417 phase transport from the surface, but absorption into polymeric or porous substrates could extend timescales
1418 (Weschler and Nazaroff, 2008). Volatility range boundaries for VOC-IVOC and IVOC-SVOC occur between C_{12}-
1419 C_{13} and C_{19}-C_{20}, respectively, for n-alkanes or compounds with equivalent volatilities. See Appendix B for
1420 calculations and Table S9.

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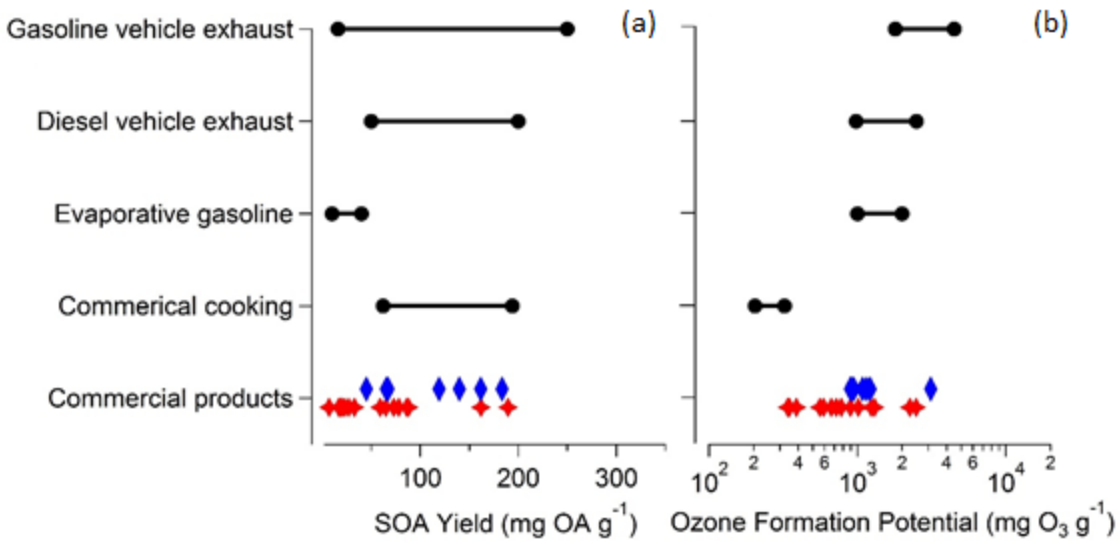

Figure 5. Comparison of (a) SOA yields and (b) Ozone formation potential of five major sources. Blue markers represent average yields of the product/process-related source categories in Figure 3, and do not include "missing" emissions. The red markers show yields of sampled consumer products calculated from speciation obtained after GC-MS analysis. All are shown as a function of mass emitted, not product composition.