



*Supplement of*

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

**Peeyush Khare and Drew R. Gentner**

*Correspondence to:* Drew R. Gentner ([drew.gentner@yale.edu](mailto:drew.gentner@yale.edu))

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.

## **S.1 Existing estimates of products/process-related VOC emissions**

Piccot et al. (1992) estimated that 7%-13% of the global non-methane volatile organic compounds were emitted from solvent use in the 1990s (Piccot et al., 1992). While, ~30% of Denmark's and Istanbul's annual anthropogenic VOC emissions are attributed to solvent use, and 5%-33% of the total ambient VOCs in Chinese studies (Lu et al., 2007; Markakis et al., 2009; Nielsen et al., 2008; Song et al., 2007). Similarly, 28% of Shanghai's (2003-2007) VOC emissions were due to solvents and other products, with industrial processes contributing another 23% and only 15% from motor vehicles (Chen et al., 2009). Studies focused on Paris found summertime, in-plume ozone formation to be VOC-sensitive in 1998-1999 where traffic and solvent emissions were the key emissions-related factors identified in a sensitivity analysis (Deguillaume et al., 2008; Menut, 2003). In the polluted and often-studied Po Valley (including Milan, Italy), a 2001 emissions inventory attributes 45% of anthropogenic VOC emissions to consumer products and commercial/industrial processes with ~40% attributed to combustion-related sources (Caserini et al., 2004). In the Po Valley and elsewhere, large observed  $\Delta\text{OA}/\Delta\text{CO}$  ratios observed at a number of sites have indicated the presence of SOA precursor contributions from non-combustion sources (incl. biogenic) (Gentner et al., 2012).

## **S.2 Additional detail on potential secondary organic aerosol (SOA) and ozone calculations**

Speciation profiles from the U.S. EPA's SPECIATE 4.4 database, the on-road Emission Factors Model (EMFAC2014) and the Almanac emissions inventory produced by the California Air Resources Board (CARB) are used to estimate chemically-speciated VOC emissions in the South Coast Air Basin (SoCAB), and statewide (California Air Resources Board, 2014; Cox et al., 2013; U.S. Environmental Protection Agency, 2014). We use the approaches in Gentner et al. (2012, 2013) to estimate SOA and ozone formation from complex mixtures of emissions. All 2347 compounds listed in the SPECIATE 4.4 database are assigned individual SOA yield values based on previous research and by applying approximations wherever necessary based on available literature (approximation rules provided in Table S6) (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). For potential ozone, the maximum ozone incremental reactivity values reported in the SAPRC07 database are assigned to individual compounds in the SPECIATE database (Carter, 2007). Overall SOA yields and ozone formation potentials for the mixture of emitted compounds from each product, or product category, are calculated via a weighted average of the ozone or SOA yields (with propagated uncertainties) for individual compounds or bins lumped by carbon number and compound class (Gentner et al., 2012, 2013).

To estimate the SOA and ozone yields from motor vehicles, we calculated exhaust and evaporative emissions from CARB's Emission Factors Model (EMFAC2014) as a function of fuel-type and LEV generation annually over the on-road vehicular fleet (Figure 1). The variation in the population and fuel use of each model type between 1990 and 2020 is also shown in Figure 1. The emissions values obtained for gasoline and diesel vehicular fleets were used in conjunction with the ozone yields given in literature (Gentner et al., 2013) to calculate total ozone from on-road gasoline and diesel motor vehicles. CARB Almanac emissions inventory and maximum ozone incremental reactivity (MOIR) values from SAPRC-07 database were used to calculate potential ozone from product/process-related sources. Where MOIR values were not available in SAPRC-07, the MOIR of an equivalent n-alkane compound based on similar volatility was used as best approximation to estimate a lower limit that allowed us to conservatively include these species in our potential ozone calculations. This was the case for only 8% of the total emissions. SOA and ozone yields from commercial cooking are estimated using the chemical speciation and emission rates provided in the national emissions inventory (NEI) on commercial cooking (U.S. Environmental Protection Agency, 2011).

### **S.3 Asphalt-related emission factor calculation**

Asphalt-related products (e.g. petroleum asphalt, liquid asphalt, asphalt cement, and asphalt binder) have a number of different CAS entries, and commercial and industrial has many formulations. Due to its production methods the bitumen in asphalt-related products contains much larger compounds with very low volatilities (not elutable in our system). One common example, petroleum asphalt (e.g. CAS 8052-42-4) is used in a wide range of commercial and industrial products and it contains a variable, unspecified mixture of compounds with boiling points that range from 150 – 1100 °C in MSDSs. This variability makes it difficult to calculate representative emission factors, and detailed emission factors (i.e. mg kg<sup>-1</sup>) of degradation byproducts are not reported in cited publications, but rather on-site or headspace concentrations due to the occupational health focus.

We were able to use the very limited data from the literature to approximate a lower estimate of the emission factor ( $EF_{asphalt}$ ) for during and immediately after the initial application of hot-mix asphalt. Experimental details can be found in referenced literature (Kriech, 2006a, 2006b). Gas-phase emissions from hot asphalt are studied using two chambers, one a batch reactor and another that spreads pre-heated asphalt in a thin layer onto a conveyor belt that moves through a sampling chamber that is supplied with zero air. Emissions determined via the batch reactor are 6-13 times greater depending on temperature, so emissions calculated via data from the conveyor system are scaled to give a more representative emission factor, albeit one that still excludes the complete lifecycle.

$$EF_{asphalt} = \frac{C_{emitted\ organic\ gas} Q_{inlet\ air} \Delta t}{Q_{asphalt\ mix} \Delta t} \quad (12)$$

Where  $C_{emitted\ organic\ gas}$ : measured concentration of emitted gas-phase organic compounds (average over entire experiment),  $Q_{inlet\ air}$ : Flow of clean, zero air into chamber,  $Q_{asphalt\ mix}$ : Flow of pre-heated hot-mix asphalt onto chamber conveyor belt,  $\Delta t$ : duration of experiment.

While the range of calculated emissions factors are similar to motor vehicle emission factors, California's asphalt use for paving and roofing is 1,540,000 tons liquid asphalt year<sup>-1</sup> (13% roofing), is much smaller than transportation fuel use (Table S4) (The Asphalt Institute, 2015). When combined with our approximate emission factor, this represents statewide I/SVOC (+VOC) emissions of 0.5 – 8 tons day<sup>-1</sup> that are not included in the inventory.

#### S.4 Discussion of anthropogenic terpenoid emissions

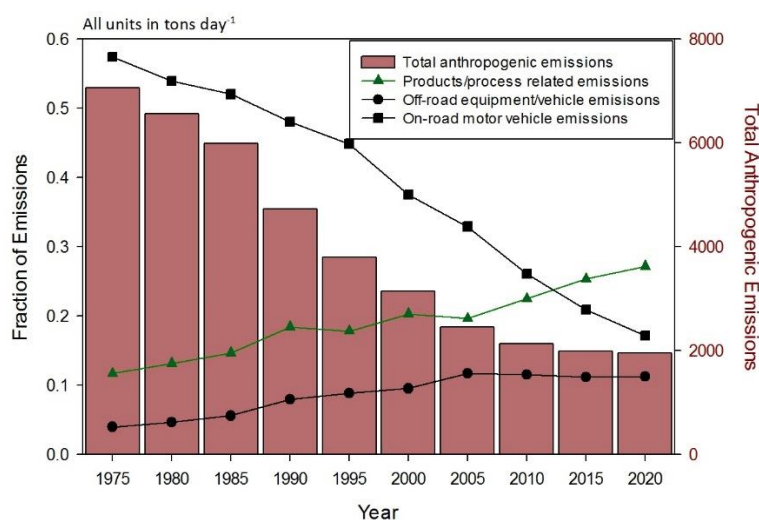
A variety of consumer products contain terpenes and other plant/biogenic oils (e.g. general purpose cleaners, disinfectants, pesticides, paints, building materials) and emit monoterpenes, other terpenes or biogenic VOCs, or byproducts from surface reactions. CARB estimates for the SoCAB are 1.9 tons day<sup>-1</sup> (esp. general purpose cleaners, disinfectants) and it is unclear to what degree all these sources are fully included in inventories. Significant terpene emissions and indoor SOA formation have also been observed off-gassing from wooden building materials, as well as “green” paint (Toftum et al., 2008). An additional 2.3 tons day<sup>-1</sup> of unspecified organics are emitted as “fragrances” used in dish/laundry soaps and a variety of additions to other household products. Fragrances, especially personal fragrance products receive exemptions from CARB VOC content limits, but still must meet reporting requirements (California Air Resources Board, 2015). While these do represent a significant emission, natural and urban biogenic sources outweigh them at an estimated 26 tons day<sup>-1</sup>.

#### S.5 SOA yield approximation rules

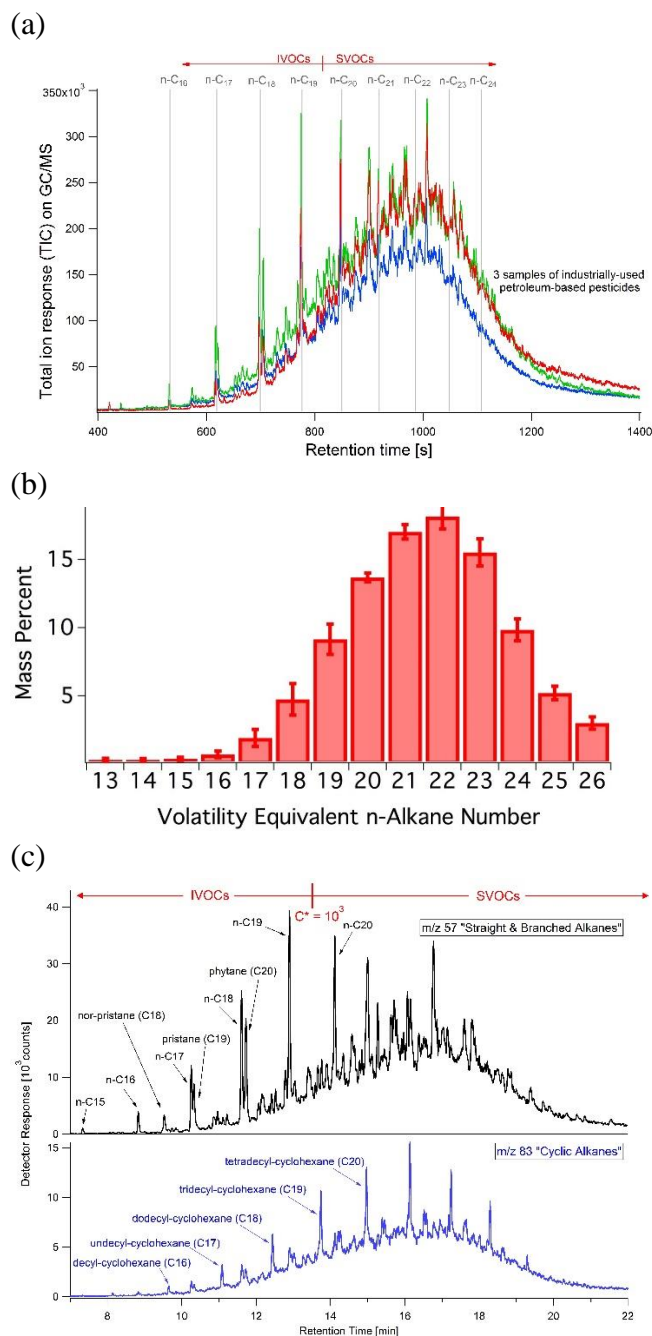
Literature SOA yields were used in this work wherever possible (Algrim and Ziemann, 2016; Chacon-Madrid et al., 2010; Chan et al., 2010; Gentner et al., 2012; Kwok and Atkinson, 1995; Ng et al., 2006; Pankow and Asher, 2008; Sadezky et al., 2006; Tsimpidi et al., 2010). The guidelines presented here are for approximation of components of the poorly-constrained and multi-faceted complex mixtures to infer the total potential SOA from the whole of these sources, and should be viewed within that context. Also, the SOA yield for any single unstudied component (studied components include toluene, xylenes, etc.) does not have a significant impact on the total

SOA potential, however unspeciated mixtures of hydrocarbons do have a larger impact and are thus treated separately. Several of the compound classes are highly uncertain (i.e. alcohols, acids, ethers, esters) since there is no prior work to base SOA yield approximations on, thus the approaches to approximate *potential* SOA yields are not applicable beyond this context.

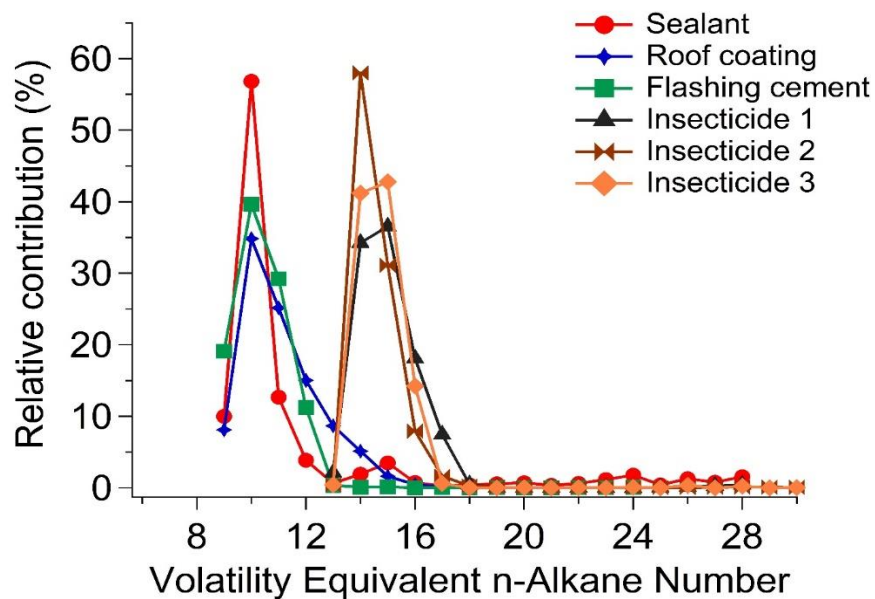
## S.6 Supplementary figures and tables



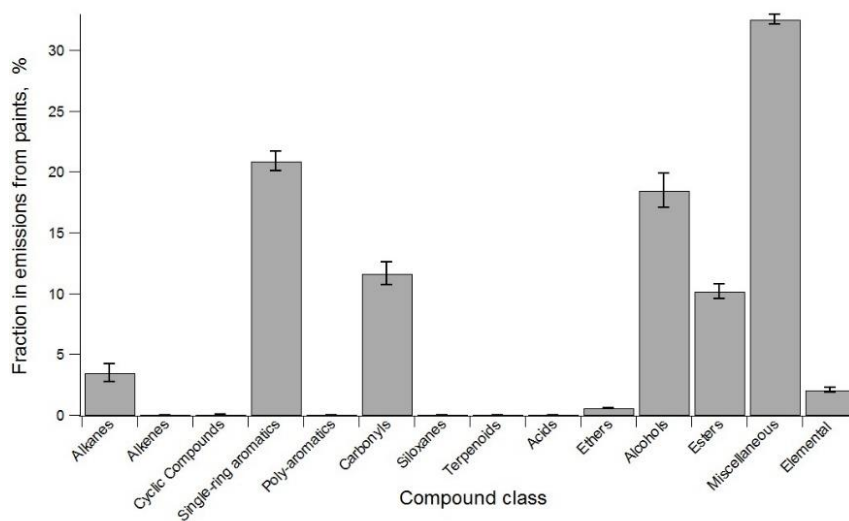
**Figure S1.** Statewide VOC emission trends in California (excluding ethane). The contribution of on-road motor vehicles to the total anthropogenic emissions has gradually declined since 1975. The contribution of product/process-related emissions show an opposite trend of gradual rise over these years.



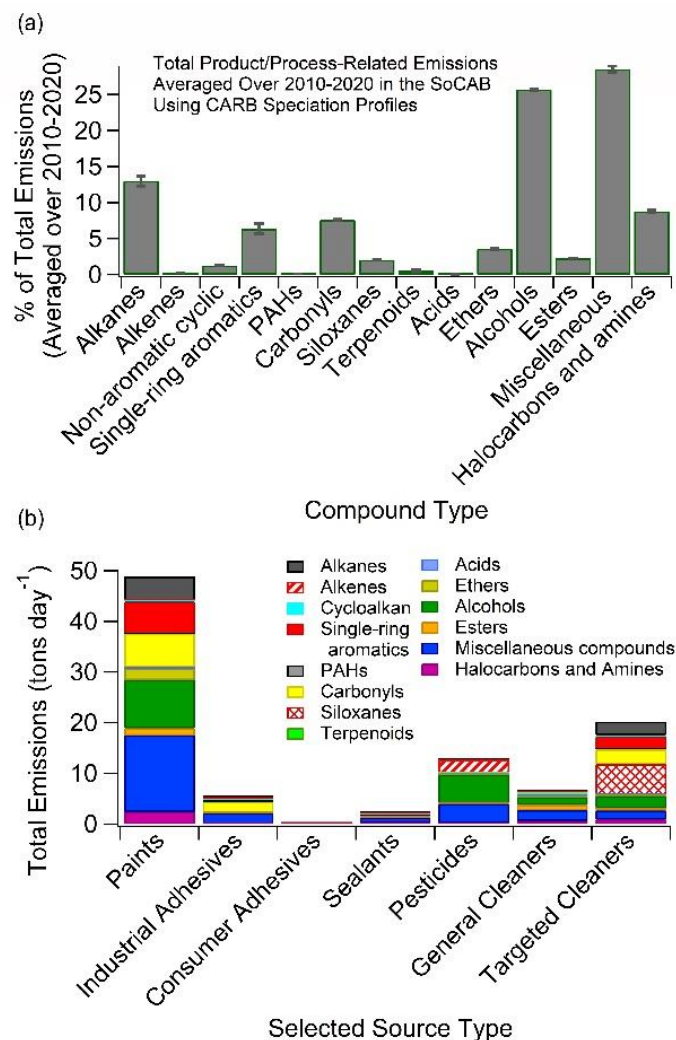
**Figure S2.** (a) Total ion chromatograms for 3 industrially used horticultural oil (i.e. petroleum-based agricultural pesticides) analyzed via GC/MS on an HP-5 column. Shown with locations of n-alkanes and an approximate boundary of IVOCs and SVOCs (at  $\sim 10 \mu\text{g m}^{-3}$ ). (b) Pesticide composition. (c) Single ion chromatograms from a petroleum-based pesticide for m/z 57 and m/z 83, typical alkane fragments that contribute more relatively to branched/straight alkanes and cyclic alkanes, respectively. Isomers of note are labeled. Such products are sprayed as water emulsions and form thin films of organics on leaves, other plant components, and surrounding soil.



**Figure S3.** Composition of sampled asphalt-related products and insecticides. The 3 asphalt-related products are primarily made up of very high molecular weight components of asphalt (non-elutable in our GC), so the fractions shown here are related to their application solvents.



**Figure S4.** Paint-related emissions (shown with standard deviation) between the years 2000-2020 based on the CARB Almanac emissions inventory and SPECIATE source profiles.



**Figure S5.** Emissions from product/process-related sources in SoCAB using the CARB emissions inventory and CARB Speciation profile database for 2010-2020 as a function of (a) compound class and (b) major product/process-related source categories in the inventory. Included for comparison to Figure 3, with minor differences that are largely attributable to changes in reporting of unspeciatiated (i.e. miscellaneous) VOC and I/SVOC emissions, including the changes in single-ring aromatics.



**Table S1.** Gas-phase emission profiles obtained from the GC-MS analysis of samples.

| Products                                | Emittable<br>fraction<br>(EF) | Mass distribution profiles |                    |                    |           |                   |                |                 |                    |       |
|---|-------------------------------|----------------------------|--------------------|--------------------|-----------|-------------------|----------------|-----------------|--------------------|-------|
|   |                               | Alkanes                    |                    |                    | Aromatics |                   |                |                 |                    | Other |
|   |                               | % of<br>EF                 | C ≤ 12<br>fraction | C > 12<br>fraction | % of EF   | C ≤ 8<br>fraction | C9<br>fraction | C10<br>fraction | C ≥ 11<br>Fraction |       |
| Naphtha cleaner                         | 100%                          | 100%                       | 100%               | -                  | -         | -                 | -              | -               | -                  | -     |
| Non-polar solvent                       | 100%                          | 7%                         | 100%               | -                  | 93%       | -                 | 100%           | -               | -                  | -     |
| Fogging Insecticide <sup>†</sup>        | 95%                           | 100%                       | -                  | 100%               | -         | -                 | -              | -               | -                  | -     |
| Semi-gloss furniture<br>coating         | 30%                           | 80%                        | 100%               | -                  | 20%       | 44%               | 56%            | -               | -                  | -     |
| Multipurpose solvent <sup>a</sup>       | 100%                          | -                          | -                  | -                  | -         | -                 | -              | -               | -                  | 100%  |
| Furniture coating <sup>†</sup>          | 40%                           | 97%                        | 100%               | -                  | 3%        | 21%               | 56%            | 23%             | -                  | -     |
| Roof paint <sup>b</sup>                 | -                             | -                          | -                  | -                  | -         | -                 | -              | -               | -                  | -     |
| Sealant <sup>c, §</sup>                 | 25%                           | 18%                        | 83%                | 17%                | 82%       | -                 | 92%            | 8%              | -                  | -     |
| Paint thinner <sup>†</sup>              | 100%                          | 97%                        | 98%                | 2%                 | 3%        | -                 | 71%            | 29%             | -                  | -     |
| Asphalt coating <sup>d, §</sup>         | 25%                           | 89%                        | 83%                | 17%                | 11%       | -                 | 78%            | 22%             | -                  | -     |
| Detergent <sup>e</sup>                  | 25%                           | -                          | -                  | -                  | 17%       | -                 | -              | -               | 100%               | 83%   |
| General purpose cleaner <sup>f, †</sup> | 3%                            | 49%                        | 31%                | 69%                | -         | -                 | -              | -               | -                  | -     |
| Multipurpose lubricant                  | 97%                           | 100%                       | 60%                | 40%                | -         | -                 | -              | -               | -                  | -     |
| Aerosol Coating Product <sup>g, †</sup> | 17%                           | 3%                         | 100%               | -                  | 72%       | 100%              | -              | -               | -                  | 25%*  |
| Flashing cement <sup>h, §</sup>         | 27%                           | 87%                        | 99%                | 1%                 | 13%       | 16%               | 43%            | 38%             | 3%                 | -     |
| Crawling Insecticide 1 <sup>i, †</sup>  | 20%                           | 100%                       | -                  | 100%               | -         | -                 | -              | -               | -                  | -     |
| Crawling Insecticide 2 <sup>j, †</sup>  | 8%                            | 100%                       | -                  | 100%               | -         | -                 | -              | -               | -                  | -     |

<sup>§</sup>Asphalt-related products.<sup>†</sup>Applied as aerosols.<sup>a</sup>Largely consists of acetone (80%) with the rest as cyclotetrasiloxanes and aryl halides.<sup>b</sup>Water based product. Other components include titanium dioxide, silica and aluminum hydroxide.<sup>c</sup>Largely consists of petroleum asphalt, clays and cellulose.<sup>d</sup>Largely consists of petroleum asphalt.<sup>e</sup>46% of the EF consists of mostly esters, 70% of which have less than 12 carbon atoms. Terpenes including limonene, eucalyptol and  $\alpha$ -terpineol form 37% of the EF.<sup>f</sup>Water-based product. Also has terpenes including camphene, d3-carene,  $\alpha$ -pinene, linalool and  $\delta$ -limonene. 60% of terpene fraction is  $\delta$ -limonene.<sup>g</sup>Contains 35% acetone and 25% hydrocarbon propellants not included in the EF. \*25% of EF is 75% acetate + 25% ketones.<sup>h</sup>Largely consists of petroleum asphalt, kaolin, cellulose and aluminum magnesium silicate.<sup>i</sup>Contains 15% hydrocarbon propellants not included in the EF.<sup>j</sup>Contains 25% hydrocarbon propellants not include in the EF.

Note: Emittable fraction is confirmed with MSDS where possible.

**Table S2.** Breakdown of potential SOA and ozone with compound classes for emissions averaged over the years 2005-2020 (based on the CARB emissions inventory and SPECIATE source profiles).

| Compound Class | Compound Class         | Potential SOA [%]    | Potential Ozone [%] |
|----------------|------------------------|----------------------|---------------------|
|                |                        |                      |                     |
| Compound Class | Alkanes                | 0.25                 | 12.07               |
|                | Alkenes                | 0.01                 | 0.91                |
|                | Non-aromatic cyclic    | 0.12 ( $\pm$ 0.19%)  | 3.04                |
|                | Single ring aromatics  | 95.33 ( $\pm$ 1.74%) | 29.16               |
|                | PAHs                   | 3.44 ( $\pm$ 4.7%)   | 0.28                |
|                | Carbonyls              | 0.00                 | 8.33                |
|                | Siloxanes              | 0.00                 | 0.00                |
|                | Terpenoids             | 0.66                 | 3.13                |
|                | Acids                  | 0.00                 | 0.06                |
|                | Ethers                 | 0.00                 | 1.24                |
|                | Alcohols               | 0.00                 | 32.92               |
|                | Esters                 | 0.00                 | 2.54                |
|                | Miscellaneous          | 0.00                 | 0.00                |
|                | Halocarbons and Amines | 0.00                 | 6.15                |
|                | Non-aromatic I/SVOCs   | 0.18                 | 0.18                |

**Table S3.** Breakdown of emissions averaged over the years 2005-2020 for major pp-source categories in as shown in Figure 3 (based on the CARB emissions inventory and SPECIATE source profiles).

| <b>Figure 3 Data</b><br>Units: tons day <sup>-1</sup> | <b>Paints</b> | <b>Industrial<br/>Adhesives</b> | <b>Consumer<br/>Adhesives</b> | <b>Sealants</b> | <b>Pesticides</b> | <b>General<br/>Cleaners</b> | <b>Targeted<br/>Cleaners</b> | <b>Total</b> |
|---|---------------|---------------------------------|-------------------------------|-----------------|-------------------|-----------------------------|------------------------------|--------------|
| Alkanes   | 2.69          | 0.27                            | 0.58                          | 0.06            | 1.02              | 0.86                        | 1.85                         | <b>7.33</b>  |
| Alkenes   | 0.00          | 0.00                            | 0.00                          | 0.00            | 0.00              | 0.00                        | 0.00                         | <b>0</b>     |
| Non-aromatic cyclic                                   | 0.02          | 0.00                            | 0.40                          | 0.00            | 0.09              | 0.00                        | 0.00                         | <b>0.51</b>  |
| Single ring aromatics                                 | 11.10         | 0.58                            | 0.14                          | 0.03            | 1.47              | 0.00                        | 2.18                         | <b>15.5</b>  |
| PAHs  | 0.01          | 0.00                            | 0.00                          | 0.00            | 0.01              | 0.00                        | 0.00                         | <b>0.02</b>  |
| Carbonyls   | 6.42          | 0.93                            | 0.60                          | 0.09            | 0.45              | 0.00                        | 3.25                         | <b>11.74</b> |
| Siloxanes   | 0.00          | 0.00                            | 0.00                          | 0.16            | 0.00              | 0.00                        | 0.15                         | <b>0.31</b>  |
| Terpenoids  | 0.00          | 0.00                            | 0.01                          | 0.00            | 0.18              | 1.30                        | 0.04                         | <b>1.53</b>  |
| Acids   | 0.00          | 0.00                            | 0.00                          | 0.00            | 0.00              | 0.12                        | 0.00                         | <b>0.12</b>  |
| Ethers  | 0.32          | 0.00                            | 0.18                          | 0.00            | 0.00              | 0.11                        | 0.12                         | <b>0.73</b>  |
| Alcohols  | 9.11          | 0.22                            | 0.06                          | 0.03            | 3.15              | 4.57                        | 3.67                         | <b>20.81</b> |
| Esters  | 5.09          | 0.00                            | 0.02                          | 0.01            | 0.00              | 0.00                        | 0.00                         | <b>5.12</b>  |
| Miscellaneous   | 16.75         | 2.19                            | 0.22                          | 0.85            | 3.09              | 0.99                        | 7.65                         | <b>31.74</b> |
| Halocarbons and<br>Amines                             | 0.50          | 0.44                            | 0.09                          | 0.00            | 0.36              | 0.19                        | 3.96                         | <b>5.54</b>  |
| Non-aromatic<br>I/SVOCs                               | 0.00          | 0.00                            | 0.00                          | 0.02            | 4.01              | 1.15                        | 0.41                         | <b>5.59</b>  |
| <b>Total</b>  | <b>52.01</b>  | <b>4.63</b>                     | <b>2.3</b>                    | <b>1.25</b>     | <b>13.83</b>      | <b>9.29</b>                 | <b>23.28</b>                 |              |

**Table S4.** Asphalt use for various paving and non-paving purposes in California and the U.S. (The Asphalt Institute, 2015).

| <u>Application</u>  | <u>2015 Usage [Thousand metric tons]</u> |              |
|---|--|--------------|
|   | CA statewide                             | U.S. Totals  |
| <b>Total Road Paving</b>                                      | <b>1220</b>                              | <b>16024</b> |
| Asphalt Cement (hot/warm-mix)                                 | 84%                                      | 76%          |
| Modified Asphalt Cement                                       | 7%                                       | 12%          |
| Cutback Asphalt   | 2%                                       | 1%           |
| Emulsified Asphalt  | 6%                                       | 10%          |
| <b>Total Non-Paving</b>                                       | <b>183</b>                               | <b>2638</b>  |
| Roofing   | >99%                                     | 89%          |
| Miscellaneous   | <1%                                      | 11%          |
| <b>Total Paving and Non-Paving</b>                            | <b>1403</b>                              | <b>18662</b> |
| Note: Asphalt usage (liquid only, does not include aggregate) |  |              |

**Table S5.** Speciation of gaseous emissions from different asphalt sources as given in SPECIATE 4.4 database. Note: The EPA and CARB also report point source emissions of larger hydrocarbons (C<sub>10</sub>+) from hot asphalt plants in the “mineral processing” category of emissions.

| <b>Asphalt Roofing: Spraying</b>            |                 | <b>Asphaltic concrete- Natural gas rotary dryer</b> |                 |
|---|-----------------|---|-----------------|
| <i>Compound name</i>                        | <i>Weight %</i> | <i>Compound name</i>                                | <i>Weight %</i> |
| n-Butane                                    | 18              | Benzene   | 4               |
| Ethane                                      | 1               | n-Butane  | 9               |
| Ethene                                      | 2               | Cyclohexane   | 1               |
| n-Heptane                                   | 14              | Formaldehyde  | 8               |
| Isomers of heptane                          | 11              | Isomers of hexane                                   | 1               |
| n-Hexane                                    | 2               | Methane   | 56              |
| Isomers of hexane                           | 12              | n-Pentane   | 6               |
| Isobutane                                   | 8               | Isomers of pentane                                  | 9               |
| Isomers of octane                           | 1               | Propane   | 4               |
| n-Pentane                                   | 18              | Toluene   | 2               |
| Propane                                     | 13              |   |                 |
| <b>Mineral products- Asphaltic concrete</b> |                 | <b>Asphaltic concrete- In place road Asphalt</b>    |                 |
| <i>Compound name</i>                        | <i>Weight %</i> | <i>Compound name</i>                                | <i>Weight %</i> |
| C-2 Alkyl indan                             | 11.21           | Benzene   | 9.5             |
| C-4 Substituted Cyclohexanone               | 2.38            | n-Butane  | 10.1            |
| C-5 Substituted Cyclohexanone               | 4.16            | 1-Butene  | 5.9             |
| C-6 Substituted Cyclohexanone               | 3.12            | C-7 Cycloparaffins                                  | 3.7             |
| n-Decane                                    | 2.87            | Ethane  | 4.6             |
| Dichloronitroaniline                        | 3.94            | Ethene  | 2               |
| n-Dodecane                                  | 18.55           | n-Hexane  | 8.8             |
| Isomers of dodecane                         | 9.59            | Isomers of hexane                                   | 8.1             |
| Methyl naphthalenes                         | 10.19           | Isobutane   | 11.2            |
| Naphthalene                                 | 6.54            | Methane   | 15.7            |
| n-Pentylcyclohexane                         | 2.04            | n-Pentane   | 5.3             |
| Isomers of tetradecane                      | 3.12            | Isomers of pentane                                  | 5.7             |
| Trimethylbenzenes (mixed)                   | 8.89            | Propane   | 5.5             |
| Trimethyldecene                             | 5.62            | 1-Propene   | 3.9             |
| n-Undecane                                  | 7.78            |   |                 |
| <b>Asphalt roofing: Tar kettle</b>          |                 |   |                 |
| <i>Compound name</i>                        | <i>Weight %</i> | <i>Compound name</i>                                | <i>Weight %</i> |
| Benzene                                     | 0.8             | Isobutane   | 0.7             |
| n-butane                                    | 11.6            | Methane   | 21.3            |
| 1-butene                                    | 7               | n-Octane  | 2.7             |
| C-7 cycloparaffins                          | 2.9             | Isomers of octane                                   | 7.4             |
| C-8 cycloparaffins                          | 0.4             | n-Pentane   | 6.3             |
| C-9 cycloparaffins                          | 1.5             | Isomers of pentane                                  | 1.1             |
| Cyclopentane                                | 2.5             | 1-Pentene   | 3.2             |
| Ethane                                      | 5.4             | Isomers of pentene                                  | 0.5             |
| Ethene                                      | 0.3             | Propane   | 10.2            |
| n-Heptane                                   | 2               | 1-Propene   | 2               |
| n-Hexane                                    | 4.9             | Toluene   | 1.9             |
| Isomers of hexane                           | 3.4             |   |                 |

**Table S6.** SOA approximation rules used to calculate potential SOA.

|  |  |
|--|--|
| <b>Alkanes and Aromatics</b>   | SOA yields are assigned based on published methods as a function of number of carbon atoms, branching, and number of rings; from Gentner et al.(Gentner et al., 2012) and the references therein.  |
| <b>Alkenes and Alkynes</b>   | <p>Treated as alkanes, such that:</p> <ul style="list-style-type: none"> <li>• Linear alkenes with less than 8 carbon atoms (and branched alkenes with less than 10 carbon atoms) are set to SOA yield of 0.</li> <li>• Linear, branched and cyclic alkenes are set to their alkane analogs for SOA yield.</li> </ul>  |
| <b>Tetracyclic and Pentacyclic Alkanes (e.g. hopanes, steranes etc.)</b> | Treated with tri-cycloalkanes.   |
| <b>Halocarbons</b>   | Non-aromatic halocarbons in the emissions calculated from SPECIATE had predominantly 1-3 carbons, and their SOA yields were estimated to be negligible.  |
| <b>Functionalized Aromatics</b>  | Conservative SOA yields for aromatic species that contain oxygen-, nitrogen-, or other containing groups are approximated as single-ring aromatics or PAHs with the same number of carbon atoms.   |
| <b>Carbonyls</b>   | SOA yields for aldehydes are shown to be small for C11 compounds and smaller, and the high-NO <sub>x</sub> SOA yield of n-tridecanal is equivalent to n-dodecane due to the preferential hydrogen abstraction from the aldehydic carbon (Chacon-Madrid et al., 2010). SOA yields for straight or branched aldehydes are set as that of the straight or branched alkane of one carbon less. SOA yields of olefinic aldehydes represent a special case where the location of the C=C double bond has a very large effect on SOA yield (Chan et al., 2010). The SOA yields of linear ketones are have been shown to be similar to that of an aldehyde of the same size and highly dependent on the position of the keto group that range from the SOA yield of the C-1 n-alkane to the C+1 n-alkane (Algrim and Ziemann, 2016; Chacon-Madrid et al., 2010). Based on these results, ketone SOA yields approximations are set to an upper and lower limit of the C+1 and C-1 n-alkane, respectively. |
| <b>Elemental compounds</b>   | All non-volatile elemental components included in the SPECIATE database (e.g. Iron, Indium, Gold) are set to SOA yield of 0.   |
| <b>Terpenoids (and other BVOCs)</b>                                      | Most terpenoid and biogenic VOC-related “compounds” included in the SPECIATE database are unspciated (e.g. pine oil, monoterpenes), except limonene and α-pinene. There is a wide array of molecular structure in monoterpene and sesquiterpene isomers (C <sub>10</sub> H <sub>16</sub> ), which greatly effects SOA yields as well as OH- vs. O <sub>3</sub> - initiated chemistry (Ng et al., 2006). All terpene-related SOA yields use the high-NO <sub>x</sub> SOA yield of 0.122 g g <sup>-1</sup> at 10 μg m <sup>-3</sup> for monoterpenes in the standard lumped model in Tsimpidi et al. (Tsimpidi et al., 2010). Other unspciated BVOC compound groups are given an upper limit of  |

---

|  |  |
|--|--|
|  | <p>0.150 g g<sup>-1</sup> to represent the lumped sesquiterpene yield in Tsimpidi et al. (Tsimpidi et al., 2010) and a lower limit of 0.12 g g<sup>-1</sup> based on the monoterpene yield.</p>  |
| <b>Alcohols</b>                                    | <p>There are no known SOA yield studies of alcohols found in the literature. Based on their vapor pressure, SOA yields are roughly approximated based on the alkane of the same structure (straight vs. branched) and vapor pressure, which equates to 4-5 more carbon atoms than the alcohol (Pankow and Asher, 2008). Alcohols are not predisposed towards fragmentation based on structure activity relationships (Kwok and Atkinson, 1995) so the lower estimate is set at the SOA yield of the C+4 alkane and the upper limit is set as the C+5 alkane.</p> |
| <b>Acids</b>                                       | <p>SOA yields from organic acids have not been explicitly studied, but they have been shown to be important intermediates to SOA formation. Similar to the approach for alcohols without robust SOA yield studies, carboxylic acids are assigned the volatility of an alkane with similar structure and volatility, with an upper value of C+8 and a lower value of C+7 (Pankow and Asher, 2008).</p>  |
| <b>Esters</b>                                      | <p>Also lacking any studies, SOA yields for esters (e.g. acetates) are approximated to the SOA yield of an alkane of similar volatility and structure, which equates to C+2 as a lower limit and C+3 as an upper limit.</p>  |
| <b>Ethers</b>                                      | <p>One SOA study has been done for ozonolysis of alkyl vinyl ethers, which is prone to fragmentation (Sadezky et al., 2006), and no published work exists for paraffinic ethers. A very approximate SOA yield is taken from alkanes of similar structure and volatility, with upper and lower limits of C+2 and C+1, respectively.</p>   |
| <b>Miscellaneous<br/>(or unspecified mixtures)</b> | <p>In several cases, emissions are unspecified (e.g. Misc. acids, Misc. low vapor pressure VOC distillates, organic carbon, undefined paraffins, Misc. proprietary VOC). The SOA yield for select, important groups is discussed in its own analysis, otherwise no specified for these groups with the exception of hydrocarbon propellants are assumed to be below C8, so SOA yield set to 0.</p>   |

---

**Table S7.** Carbon isotope analysis results of twelve commercially available consumer products. Also given are the weight fractions of IVOCs and aromatic compounds found in individual products. Please see Table S1 for detailed mass distribution profiles.

| Product name                 | $\delta^{13}\text{C}$<br>(‰) | $\Delta^{14}\text{C}$<br>(‰) | Fraction<br>Modern  | $^{14}\text{C}$ age<br>(Before<br>present) | IVOCs<br>% | Aromatics<br>% | Emittable<br>Fraction |
|------------------------------|------------------------------|------------------------------|---------------------|--|------------|----------------|-----------------------|
| Naphtha cleaner              | $-29.0 \pm 0.1$              | $-999.4 \pm 0.5$             | $0.0006 \pm 0.0005$ | $>51700$                                   | -          | -              | 100%                  |
| Non-polar solvent            | $-27.4 \pm 0.1$              | $-998.5 \pm 0.5$             | $0.0015 \pm 0.0005$ | $52200 \pm 2800$                           | -          | 93%            | 100%                  |
| Fogging Insecticide***       | $-26.7 \pm 0.1$              | $-999.1 \pm 0.5$             | $0.0009 \pm 0.0005$ | $>50300$                                   | 95%        | -              | 95%                   |
| Semi-gloss furniture coating | $-29.9 \pm 0.1$              | $-565.4 \pm 0.7$             | $0.4381 \pm 0.0007$ | $6630 \pm 15$                              | -          | 6%             | 30%                   |
| Multipurpose solvent         | $-30.6 \pm 0.1$              | $-997.8 \pm 0.7$             | $0.0022 \pm 0.0007$ | $49300 \pm 2700$                           | -          | -              | 100%                  |
| Furniture coating***         | $-30.2 \pm 0.1$              | $-650.0 \pm 0.6$             | $0.3528 \pm 0.0006$ | $8370 \pm 15$                              | -          | 1%             | 40%                   |
| Roof paint                   | $-22.7 \pm 0.1$              | $-985.0 \pm 0.5$             | $0.0151 \pm 0.0005$ | $33690 \pm 280$                            | -          | -              | -                     |
| Sealant**                    | $-27.4 \pm 0.1$              | $-969.9 \pm 0.5$             | $0.0303 \pm 0.0005$ | $28080 \pm 140$                            | 0.77%      | 21%            | 25%                   |
| Paint thinner***             | $-29.1 \pm 0.1$              | $-999.7 \pm 0.5$             | $0.0003 \pm 0.0005$ | $>53400$                                   | 2%         | 3%             | 100%                  |
| Asphalt coating**            | $-27.6 \pm 0.1$              | $-994.8 \pm 0.6$             | $0.0052 \pm 0.0006$ | $42200 \pm 970$                            | 4%         | 3%             | 25%                   |
| Detergent                    | $-27.9 \pm 0.1$              | $-807.8 \pm 0.6$             | $0.1938 \pm 0.0006$ | $13180 \pm 25$                             | 3.5%       | 4%             | 25%                   |
| General purpose cleaner***   | $-27.7 \pm 0.1$              | $-811.1 \pm 1.3$             | $0.1904 \pm 0.0013$ | $13320 \pm 60$                             | 1%         | -              | 3%                    |
| Multipurpose lubricant       | -                            | -                            | -                   | -  | 39%        | -              | 97%                   |
| Aerosol Coating Product***   | -                            | -                            | -                   | -  | -          | 12%            | 17%                   |
| Flashing cement**            | -                            | -                            | -                   | -  | 0.2%       | 3.5%           | 27%                   |
| Crawling Insecticide 1***    | -                            | -                            | -                   | -  | 20%        | -              | 20%                   |
| Crawling Insecticide 2***    | -                            | -                            | -                   | -  | 8%         | -              | 8%                    |

\*Crude oil and plant derived ethanol were used for multiple reference blanks. (Please see SI.)

\*\*Asphalt related products.

\*\*\*Applied as aerosols.



**\*Table S8.** Carbon isotope analysis results of the reference blanks.

| <b>Reference mixtures</b> | <b><math>\delta^{13}\text{C}</math> (‰)</b> | <b><math>\Delta^{14}\text{C}</math> (‰)</b> | <b>Fraction Modern</b> | <b><math>^{14}\text{C}</math> age (BP)</b> |
|---------------------------|---|---|------------------------|--|
| Blank1 EtOH               |   | $10.8 \pm 1.7$                              | $1.0189 \pm 0.0017$    | $-145 \pm 15$                              |
| Blank1 EtOH .27mgC        |   | $10.2 \pm 1.4$                              | $1.0183 \pm 0.0014$    | $-140 \pm 15$                              |
| Blank 2 EtOH              | $-12 \pm 0.1$                               | $12.0 \pm 1.7$                              | $1.0202 \pm 0.0017$    | $-155 \pm 15$                              |
| Blank 2 EtOH .10mgC       |   | $7.6 \pm 2.4$                               | $1.0157 \pm 0.0024$    | $-120 \pm 20$                              |
| Blank 2 EtOH .21mgC       |   | $10.1 \pm 1.4$                              | $1.0182 \pm 0.0014$    | $-140 \pm 15$                              |
| Blank 3 crude oil .040mgC |   | $-958.4 \pm 1.2$                            | $0.0419 \pm 0.0012$    | $25490 \pm 230$                            |
| Blank 4 crude oil         | $-27 \pm 0.1$                               | $-983.8 \pm 0.1$                            | $0.0163 \pm 0.0001$    | $33060 \pm 60$                             |
| Blank 4 crude oil .10mgC  |   | $-982.0 \pm 0.2$                            | $0.0182 \pm 0.0002$    | $32200 \pm 100$                            |

**Table S9:** Emission timescales (summarized in Figure 4). Note: Timescale ranges are based on emission velocities for outdoor environments ( $v_e = 50 - 10 \text{ m hr}^{-1}$ ). See Appendix B text on emission timescales calculation for further details.  $K_{OA}$  is calculated using the SPARC online calculator (ARChem) at 25 °C and 1 atm.

| Compounds<br>w/ Carbon<br>numbers   | Octanol-air<br>partitioning<br>coefficient (log<br>$K_{OA}$ ) | Lifetime<br>(1 mm layer)<br>[hr.] | Lifetime<br>(0.1 mm layer)<br>[hr.] | Lifetime<br>(0.01 mm layer)<br>[hr.] |
|---|---|-----------------------------------|-------------------------------------|--------------------------------------|
| <b>n-alkanes (or alkane of equivalent volatility)</b>   |   |                                   |                                     |                                      |
| <i>Approximate VOC Range (<math>C^* \geq 3.2 \times 10^6 \mu\text{g m}^{-3}</math>)</i>               |   |                                   |                                     |                                      |
| 4   | 1.4   | 5.4E-04 – 2.7E-03                 | 5.4E-05 – 2.7E-04                   | 5.4E-06 – 2.7E-05                    |
| 5   | 1.9   | 1.4E-03 – 7.2E-03                 | 1.4E-04 – 7.2E-04                   | 1.4E-05 – 7.2E-05                    |
| 6   | 2.3   | 4.0E-03 – 2.0E-02                 | 4.0E-04 – 2.0E-03                   | 4.0E-05 – 2.0E-04                    |
| 7   | 2.7   | 1.1E-02 – 5.5E-02                 | 1.1E-03 – 5.5E-03                   | 1.1E-04 – 5.5E-04                    |
| 8   | 3.2   | 3.1E-02 – 1.5E-01                 | 3.1E-03 – 1.5E-02                   | 3.1E-04 – 1.5E-03                    |
| 9   | 3.6   | 8.7E-02 – 4.4E-01                 | 8.7E-03 – 4.4E-02                   | 8.7E-04 – 4.4E-03                    |
| 10  | 4.1   | 2.5E-01 – 1.2E+00                 | 2.5E-02 – 1.2E-01                   | 2.5E-03 – 1.2E-02                    |
| 11  | 4.6   | 7.1E-01 – 3.5E+00                 | 7.1E-02 – 3.5E-01                   | 7.1E-03 – 3.5E-02                    |
| 12  | 5.0   | 2.0E+00 – 1.0E+01                 | 2.0E-01 – 1.0E+00                   | 2.0E-02 – 1.0E-01                    |
| <i>Approximate IVOC Range (<math>320 &lt; C^* &lt; 3.2 \times 10^6 \mu\text{g m}^{-3}</math>)</i>     |   |                                   |                                     |                                      |
| 13  | 5.5   | 5.9E+00 – 3.0E+01                 | 5.9E-01 – 3.0E+00                   | 5.9E-02 – 3.0E-01                    |
| 14  | 5.9   | 1.7E+01 – 8.5E+01                 | 1.7E+00 – 8.5E+00                   | 1.7E-01 – 8.5E-01                    |
| 15  | 6.4   | 5.0E+01 – 2.5E+02                 | 5.0E+00 – 2.5E+01                   | 5.0E-01 – 2.5E+00                    |
| 16  | 6.9   | 1.4E+02 – 7.2E+02                 | 1.4E+01 – 7.2E+01                   | 1.4E+00 – 7.2E+00                    |
| 17  | 7.3   | 4.3E+02 – 2.1E+03                 | 4.3E+01 – 2.1E+02                   | 4.3E+00 – 2.1E+01                    |
| 18  | 7.8   | 1.3E+03 – 6.3E+03                 | 1.3E+02 – 6.3E+02                   | 1.3E+01 – 6.3E+01                    |
| 19  | 8.3   | 3.6E+03 – 1.8E+04                 | 3.6E+02 – 1.8E+03                   | 3.6E+01 – 1.8E+02                    |
| <i>Approximate SVOC Range (<math>0.32 &lt; C^* &lt; 320 \mu\text{g m}^{-3}</math>)</i>                |   |                                   |                                     |                                      |
| 20  | 8.7   | 1.1E+04 – 5.4E+04                 | 1.1E+03 – 5.4E+03                   | 1.1E+02 – 5.4E+02                    |
| 21  | 9.2   | 3.2E+04 – 1.6E+05                 | 3.2E+03 – 1.6E+04                   | 3.2E+02 – 1.6E+03                    |
| 22  | 9.7   | 9.4E+04 – 4.7E+05                 | 9.4E+03 – 4.7E+04                   | 9.4E+02 – 4.7E+03                    |
| 23  | 10.1  | 2.8E+05 – 1.4E+06                 | 2.8E+04 – 1.4E+05                   | 2.8E+03 – 1.4E+04                    |
| 24  | 10.6  | 8.1E+05 – 4.1E+06                 | 8.1E+04 – 4.1E+05                   | 8.1E+03 – 4.1E+04                    |
| 25  | 11.1  | 2.5E+06 – 1.2E+07                 | 2.5E+05 – 1.2E+06                   | 2.5E+04 – 1.2E+05                    |
| 26  | 11.6  | 7.3E+06 – 3.6E+07                 | 7.3E+05 – 3.6E+06                   | 7.3E+04 – 3.6E+05                    |
| <i>Approximate LVOC Range (<math>3.2 \times 10^{-4} &lt; C^* &lt; 0.32 \mu\text{g m}^{-3}</math>)</i> |   |                                   |                                     |                                      |
| 27  | 12.0  | 2.1E+07 – 1.1E+08                 | 2.1E+06 – 1.1E+07                   | 2.1E+05 – 1.1E+06                    |
| 28  | 12.5  | 6.3E+07 – 3.2E+08                 | 6.3E+06 – 3.2E+07                   | 6.3E+05 – 3.2E+06                    |
| <b>Aromatics</b>  |   |                                   |                                     |                                      |
| 6   | 2.7   | 9.4E-03 – 4.7E-02                 | 9.4E-04 – 4.7E-03                   | 9.4E-05 – 4.7E-04                    |
| 7   | 3.2   | 3.1E-02 – 1.5E-01                 | 3.1E-03 – 1.5E-02                   | 3.1E-04 – 1.5E-03                    |
| 8   | 3.6   | 8.5E-02 – 4.3E-01                 | 8.5E-03 – 4.3E-02                   | 8.5E-04 – 4.3E-03                    |
| 9   | 4.1   | 2.4E-01 – 1.2E+00                 | 2.4E-02 – 1.2E-01                   | 2.4E-03 – 1.2E-02                    |
| 10  | 4.5   | 6.9E-01 – 3.5E+00                 | 6.9E-02 – 3.5E-01                   | 6.9E-03 – 3.5E-02                    |
| 11  | 5.0   | 2.0E+00 – 1.0E+01                 | 2.0E-01 – 1.0E+00                   | 2.0E-02 – 1.0E-01                    |
| 12  | 5.5   | 5.8E+00 – 2.9E+01                 | 5.8E-01 – 2.9E+00                   | 5.8E-02 – 2.9E-01                    |
| 13  | 5.9   | 1.7E+01 – 8.5E+01                 | 1.7E+00 – 8.5E+00                   | 1.7E-01 – 8.5E-01                    |
| 14  | 6.4   | 5.0E+01 – 2.5E+02                 | 5.0E+00 – 2.5E+01                   | 5.0E-01 – 2.5E+00                    |
| <b>Other</b>  |   |                                   |                                     |                                      |
| ethanol   | 3.2   | 3.4E-02 – 1.7E-01                 | 3.4E-03 – 1.7E-02                   | 3.4E-04 – 1.7E-03                    |
| ethylene glycol   | 4.9   | 1.5E+00 – 7.4E+00                 | 1.5E-01 – 7.4E-01                   | 1.5E-02 – 7.4E-02                    |
| acetone   | 2.8   | 1.4E-02 – 6.9E-02                 | 1.4E-03 – 6.9E-03                   | 1.4E-04 – 6.9E-04                    |

**References (SI-only, all other references are consistent with main text)**

Kriech, A. J.: Comparison of straight run vacuum distilled bitumen and semi-blown bitumen (Heritage Research Group)., 2006a.

Kriech, A. J.: Bitumen fume composition as a function of binder temperature- Physical and chemical analysis of binder fumes at various relevant temperatures using two different laboratory fume generation techniques. (Heritage Research Group)., 2006b.