Watching Paint Dry: I/VOC Emissions from Architectural Coatings and their Impact on SOA Formation

Rebecca Tanzer-Gruener,[1] Liam D. Dugan,[2] Mark E. Bier,[2] Allen L. Robinson[1] Albert A. Presto[1,]*

[1]Center for Atmospheric Particle Studies and Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA, USA

[2]Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA

*Corresponding author: apresto@andrew.cmu.edu

Abstract

Emissions from volatile chemical products (VCPs) are emerging as a major source of anthropogenic secondary organic aerosol (SOA) precursors. Paints and coatings are an important class of VCPs that emit both volatile and intermediate volatility organic compounds (VOCs and IVOCs). In this study, we directly measured I/VOC emissions from representative water-based (latex) and oil paints used in the U.S. Paint I/VOC emissions vary over several orders of magnitude by both solvent and gloss level. Oil paint had the highest emissions ($>10^5$ µg/g-paint) whereas low-gloss interior paints (Flat, Satin, and Semigloss) all emitted ~10^2 µg/g-paint. Emissions from interior paints are dominated by VOCs, whereas exterior-use paints emitted a larger fraction of IVOCs. Extended emissions tests showed that most I/VOC emissions occur within 12-24 hours after paint application, though some IVOC-dominated paints continue to emit for 48 hours or more. We used the emissions measurements to estimate paint I/VOC emissions and subsequent SOA production in the U.S. Total annual paint I/VOC emissions are 168 +/- 15 Mg. This amounts to 291 g/kg of paint used and 0.51 kg/person, which are significantly larger than comparable emissions factors from combustion systems. These emissions contribute to the formation of 8 Mg of SOA annually. Oil paints contribute ~90% of the I/VOC emissions and SOA formation, even though it only accounts for ~20% of paint usage.

Synopsis

We find that paints are a major source of organic vapor emissions. Atmospheric oxidation of these paint vapors is an important source of particulate matter.

1 Introduction

PM$_{2.5}$, particulate matter with a diameter of less than 2.5 micrometers, has deleterious effects on human health and the environment.[1,2] Exposure to elevated concentrations of PM$_{2.5}$ is linked to increased risk of respiratory and cardiovascular disease, making poor air quality one of the leading preventable causes of death worldwide.[3]

A significant portion of PM$_{2.5}$ mass (20-90%) is organic aerosol (OA). OA can be further classified as either primary (POA) or secondary (SOA).[4] SOA forms through reactions in the atmosphere and makes up a significant portion of ambient OA even in urban areas.[5–8] SOA can be formed when pollutants which are emitted as vapors such as volatile organic compounds (VOCs) react with oxidants and the subsequent products condense into the particle phase. Here we define VOCs as organic compounds with effective saturation concentrations (C*) greater than 3.2×10^6 μg/m^3. Less volatile Intermediate Volatile Organic Compounds (IVOCs, $3.2 \times 10^6 \geq$ C* $\geq 3.2 \times 10^2$ μg/m^3) also can be important SOA precursors,[9–11] potentially contributing as much as 50% of urban SOA.[12]

Historically, mobile sources have been a large source of anthropogenic SOA precursors. However, as vehicles have become cleaner due to regulations and new technologies[13] the importance of SOA formation from non-combustion volatile chemical products (VCPs) has increased.[14,15] VCPs contribute about a quarter of VOC emissions in the U.S.; that is about twice as much as diesel and gasoline exhaust emissions combined.[14] The majority of research on anthropogenic sources of SOA has focused on emissions from combustion processes[16–18] despite the fact that VCPs are thought to have significant SOA yields.[19] In order to address this gap, we need to quantify the magnitude and composition of SOA-forming emissions from VCPs.

One challenge for understanding emissions from VCPs is that these products cover a wide range of forms and functions including cleaning supplies, personal care products, paints and coatings, and many other products. Emissions from some of these products are more atmospherically relevant than others due to their timescales and modes of emission. Paints and coatings, which made up 13% of the U.S. organic solvent consumption for 2012, are thought to play a significant role in contributing to VOC emissions, with estimated emissions of > 50 tons per day.[14,15] Seltzer et al. recently estimated paints and coatings contribute 33% of VCP VOC emissions in the United States.[20]

Although many previous studies have characterized paint emissions[21–25] there has been little effort to understand their contribution to SOA formation. For example previous studies have quantified emissions of hazardous VOCs,[24,26,27] emissions of individual VOCs,[28–30] their impact on indoor air quality,[31] and research on outdoor ozone reactivity.[32] Recent research hypothesizes that paints could be an important source of SOA precursors. However, we are not aware of any published experimental work that has quantified I/VOC (IVOC + VOC) emissions from paints and their contribution to SOA formation. This paper describes an experimental study of I/VOC emissions from a wide range of architectural coatings. Ultimately, we calculate the contribution of architectural coatings to VOC concentrations and SOA formation potential in the U.S.

2 Instrumentation and Methods

2.1 Materials

The paint sector is very large. Under the US Census Bureau's classification of "architectural coatings" (category#: 3255101) the mass of paints used per year, scaled to the 2021 population, is 3.1 Tg.[33] Variability across this large sector stemming from differences in

81 solvent (water versus oil), manufacturer, gloss level (high through low), indoor vs outdoor, etc.

82 One of the major differentiators between paints are whether they are oil (alkyd) or water

83 (acrylic/latex) based. Fifty years ago, most paints were oil-based because of their great resistance

84 to wear and ease of application.[34] However, oil-based paints contain much higher levels of

85 VOCs, and over the past few decades there has been a dramatic shift to water-based paints.[34] In

86 general water-based paints have <250 g/L of VOCs while oil-based paints are required to have

87 <380 g/L of VOCs.[35] There are also "low-VOC" paints which are required to have <5 g/L of

88 VOCs. It is important to note that these requirements are tied to the VOCs in the solvent portion

89 of the paints and does not account for additional solvents that are used in the pigments and

90 binders.

91   Our approach was to sample across as much of this phase space as possible. The Census

92 Bureau inventory includes 23 classifications of paint which can be grouped into five categories

93 of latex paint (Flat, Semi-gloss Interior [SemiInt], Semi-gloss Exterior [SemiExt], High Gloss,

94 and Satin) and oil-based paint. We tested commercially available paints from each of those

95 categories. A full description of the paints selected can be found in Table S1 in the SI.

96 **2.2 Procedures**
97
98   We conducted two types of experiments with each of the paints: (1) a headspace sample

99 and (2) an extended emission experiment. Each of these experiment types are described in detail

100 below. During extended emissions testing, each paint sample was applied to an approximately 58

101 cm^2 piece of drywall. Drywall was selected as the painting material as it is a commonly painted

102 surface material throughout the United States.

103   Headspace experiments were used to obtain a fingerprint of paint vapors. In these

104   experiments we sampled directly (~5 cm) above open paint cans that were placed in a fume

105   hood. Figure S1 shows a schematic of the headspace experimental setup.

106   Extended emission experiments used a 1.2 L aluminum flux chamber (Figure S1). At the

107   start of each extended emission experiment a piece of pre-cut drywall was weighed. Following

108   weighing the drywall was painted, re-weighed to determine the mass of the paint applied, and

109   immediately placed into the chamber. As shown in Table S2, most experiments used ~0.7 – 2 g

110   of paint. The chamber was then sealed, and sampling began. VOC-filtered air was pulled through

111   the flux chamber at a flowrate of 0.37 slpm. This gave a residence time of 3.2 minutes.

112   We used multiple methods to comprehensively quantify the composition of paint I/VOCs

113   in both the headspace and extended emissions experiments. VOCs and more volatile IVOCs

114   (e.g., naphthalene) were measured with a quadrupole PTR-MS (Proton Transfer Reaction Mass

115   Spectrometer).[36] The PTR-MS was operated in scan mode from m/z 21 to 155 and sampled

116   continuously for the entirety of the extended emissions tests (typically 48 hours).

117   IVOCs were primarily quantified using Tenax sorbent tubes followed by thermal

118   desorption GC-MS (gas chromatography-mass spectrometry) analysis. Tenax TA was selected as

119   the sorbent material because it performs well while sampling in high moisture environments and

120   is known to be effective at measuring I/VOCs.[37–39] A full description of the GC-MS system as

121   well as sorbent tube cleaning and analysis procedures can be found description section S.3 in the

122   SI.

123   Tenax tube samples were collected over one-hour intervals. Tenax tubes were collected

124   during approximately hours 0-1, 1-2 hours, 4-5 hours, 8-9 hours, after 24 hours, and 48 hours

125   after paint application. Table S2 in the SI shows the exact sampling times for each experiment.

2.3 Analysis and Compound Identification
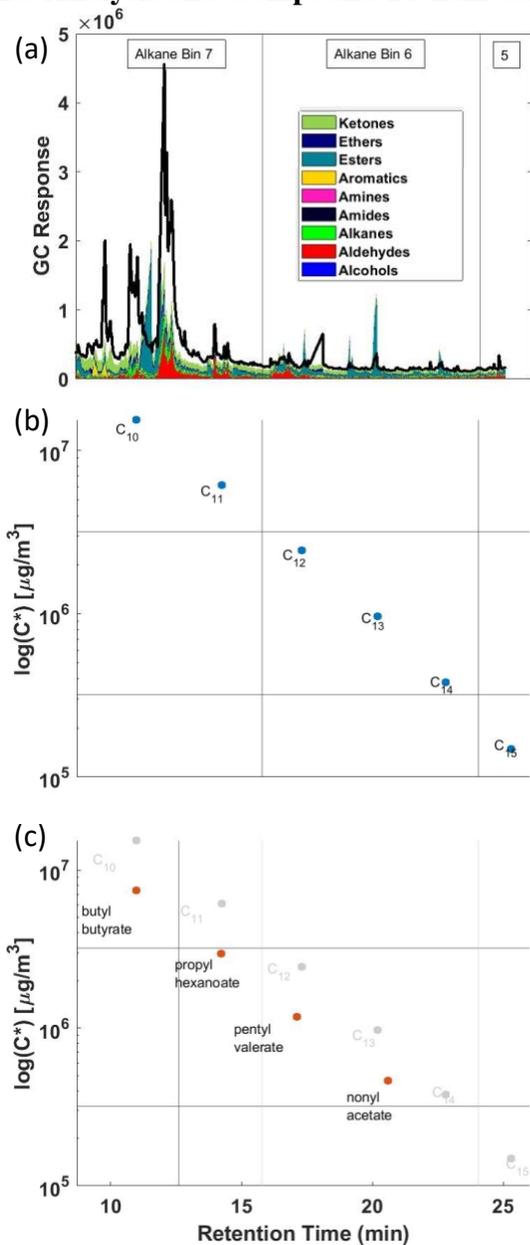
Figure 1. Volatility binning and compound class grouping. (a) The total ion chromatograph of a Satin headspace sample is shown by the thick black line. Signal decomposed into compound class contributions using marker ions is shown with the colored shading. Vertical lines show logarithmically spaced C^* bins determined from alkane volatility (e.g., Alkane Bin 7 corresponds to the $C^* = 10^7$ $\mu g/m^3$ bin). The relationship between retention time and volatility is shown for a series of n-alkanes (b) and esters (c). Panel (c) also shows the alkanes as light points to highlight the offset in ester volatility relative to alkanes.

137   To estimate the SOA formation potential of paint emissions, we need to quantify the

138   I/VOC emissions by both volatility (C*) and composition. We did this by combining data from

139   the PTR-MS and GC-MS to comprehensively characterize the total I/VOC emissions per mass of

140   paint applied for all six of the tested paint types.

141   A challenge is that the complexity of paint emissions makes them hard to speciate at the

142   molecular level. For example, IVOCs captured on the Tenax sorbent tubes cannot be fully

143   speciated using traditional one-dimensional gas chromatography. Instead, most of the GC signal

144   appears as an unresolved complex mixture (UCM). An example chromatograph is shown in

145   Figure 1a. There are few well-defined peaks. Instead, most of the mass elutes as a broad UCM

146   hump. Since SOA formation depends on volatility and molecular structure, one must quantify the

147   total mass of emissions with enough chemical specificity to estimate SOA yields.

148   **Analysis of GC-MS data.** We need to characterize both the volatility and the chemical

149   nature of the UCM. We use GC elution time to characterize volatility and the mass spectral data

150   to characterize chemical composition. Previous work has used GC-MS analysis to quantify UCM

151   emissions from combustion systems.[40,41] We draw on and expand those methods here.

152   Previous work has used the retention time-volatility relationship to map the UCM to the

153   volatility basis set for combustion emissions.[42,43] An example of this binning is shown in Figure

154   1b for a series of n-alkanes. There is a nearly linear relationship between log(C*) and alkane

155   retention time. This relationship can in turn be used to classify UCM into logarithmically spaced

156   C* bins, which are shown as vertical lines in Figure 1a and b.

157   IVOC emissions from combustion systems are generally dominated by aliphatic and

158   aromatic hydrocarbons.[44] Since variations in hydrocarbon volatility are mostly a function of

159   carbon number (rather than molecular structure),[45] in previous work a single relationship

160 between retention time and volatility has been sufficient. However, paint emissions contain

161 other, often more polar, compound classes (e.g., ketones, aldehydes, alcohols, and esters) that

162 may have different relationships between C^* and retention time. Therefore, mapping the GC-MS

163 signal into C^* bins requires classifying the UCM by composition.

164 An example of a different C^*-retention time relationship is shown for a series of esters in

165 Figure 1c. While retention time and C^* show a log-linear relationship for the esters, the esters are

166 offset relative to the alkanes. This means that we cannot use the C^* bins defined by alkane

167 retention times for the esters; hence Figure 1c shows different boundaries for the C^* bins for

168 esters. Thus, in order to bin the UCM mass emitted from the paints, we need to separately

169 quantify volatility for each compound class of interest. We calibrated the C^*-retention time

170 relationship for nine classes of compounds (alcohols, aldehydes, alkanes, amides, amines,

171 aromatics, esters, ethers, and ketones) and defined separate retention time windows for each C^*

172 bin. Full details are presented in Table S3.

173 Since the relationship between C^* and retention time varies by compound class, mapping

174 the UCM volatility also requires apportioning the GC signal into the nine compound classes

175 shown in Figure 1a. This was done using marker ions in the mass spectra. We identified marker

176 ions using two basic rules: (1) the marker needed to be unique, or nearly unique, to the

177 compound class of interest and (2) the marker ion needed to make up a non-trivial amount

178 (ideally >5%) of the overall signal for the compound class.

179 While there are common marker ions routinely used to interpret mass spectra,[46] they are

180 not necessarily appropriate for use in our analysis given the complexity of the signal. For

181 example, *m/z* 57 is a common marker ion for hydrocarbons, but it is a poor marker ion for our

182 samples because *m/z* 57 appears in the mass spectrum for nearly every molecule with a long

183   carbon chain. Therefore, it is not specific enough to use as a marker ion for paint analysis.

184   Instead, we used the NIST mass spectral library to determine marker ions for each of our nine

185   compound classes. Marker ions and the percent contribution to their compound class are listed in

186   Table S4.

187   The GC-MS signal was therefore classified by both compound class and volatility. We

188   extracted the signal for each marker ion and scaled it by the corresponding volatility-dependent

189   multiplier from Table S4. Signal was subsequently converted to mass using calibrations from

190   compound class and volatility bin specific representative compounds (Table S3). Volatility was

191   then apportioned using the predefined volatility bins described above. The net result of this

192   analysis is shown in Figure 1a, where the colors indicate contribution of different compound

193   classes. Any unapportioned signal (the white area in Figure 1a) was assumed to have the same

194   volatility relationship and mass calibration as alkanes. GC-MS data for the headspace samples of

195   each paint type can be found in Figure S3.

196   **Analysis of PTR-MS data.** Our PTR-MS has unit mass resolution. It therefore is unable

197   to separate isobaric ions, nor can it distinguish between compounds with the same elemental

198   composition. We addressed this in several ways, as detailed below.

199   For most mass fragments compound identification relied on the PTR-MS library[47] to

200   identify possible compounds for a given m/z. One exception was for m/z 45. This ion is

201   traditionally identified as acetaldehyde, but it has been suggested that it is likely ethylene glycol

202   in paint emissions.[23] For some mass-to-charge ratios there is only one suggested compound in

203   the PTR-MS library, however there are many other mass-to-charge ratios which may have

204   contributions from multiple compounds. For those m/z a search on PubChem was conducted to

205   identify the most likely of the suggested compounds to be found in paints.

206   Not all mass-to-charge ratios that were detected in the PTR-MS were able to be identified

207   with the combination of the PTR-MS Library and PubChem. To aid in the identification, an open

208   headspace analysis of the paint samples was conducted with a high resolution ThermoFisher

209   Scientific Exactive Plus Extended Mass Range (EMR) mass spectrometer. The orbitrap, operated

210   in the normal mass range, allowed for exact mass measurements using a resolution of 140,000 at

211   *m/z* 200. A custom atmospheric pressure chemical ionization (APCI) setup operated at 1400 V

212   was used to generate the ions from the paint emissions. To improve the mass accuracy of

213   detected species, a lock mass calibration technique was utilized. The orbitrap data allowed us to

214   better constrain isobaric species that could not be separated by the PTR-MS. Table S5 shows a

215   full list of ions scanned by the PTR-MS, the compound assigned to that *m/z*, and the resources

216   used to make that determination (PTR library, PubChem, and/or ACPI Orbitrap).

217   Following complete identification of compounds measured by the PTR-MS with the help

218   of the EMR measurements, the emissions were also classified into one of the nine compound

219   groups just as the GC-MS measurements were. Effective saturation concentrations (C*) were

220   calculated for each group using the SIMPOL method[45] to identify compounds as either IVOCs or

221   VOCs. Ultimately masses of I/VOCs measured by both the GC-MS and PTR-MS were added

222   together to obtain total I/VOC emissions per mass of paint applied (µg/g) for the tested paint

223   types.

3 Results and Discussion

3.1 Total Emissions

228   Figure 2 shows the results for the total mass emitted per mass of paint applied (µg/g) over

229   48 hours during the extended emissions tests for each of the six paint types tested. Figure 2a

230   shows the total emissions split among VOCs and IVOCs, and Figure 2b shows emissions by

231   compound class.
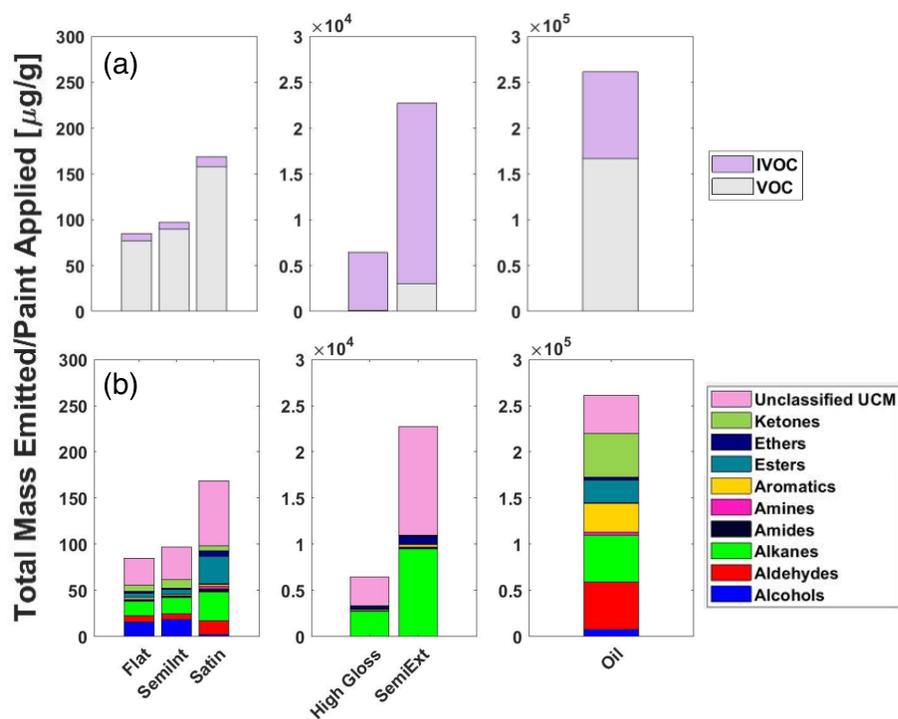
Figure 2. *Total I/VOC emissions (µg/g-paint) over two-day extended emissions experiments. Based on repeat experiments the uncertainty of the total mass measured is +/- 9%. Panel (a) separates the emissions into IVOC and VOC and (b) separates by compound class. The magnitude and composition of emissions differ between the indoor, low-gloss paints (Flat, SemiInt, and Satin), the higher gloss paints (High Gloss and SemiExt), and the oil-based paint (Oil). The lower gloss paints emit mostly alkanes, alcohols, and aldehydes while the oil-based paint emits aldehydes, alkanes, and aromatics.*

234   Total I/VOC emissions varied by several orders of magnitude across the paint types.

235   I/VOCs emitted from the low-gloss, indoor, water-based paints (Flat, SemiInt, and Satin) are on

236   the order of 10^2 µg/g of paint applied. The higher gloss, water-based paints emitted ~10^4 µg/g of

237   I/VOC. The oil-based paint emitted >10^5 µg/g of paint. This indicates that representing paint

238   I/VOC emissions in chemical transport models (CTMs) will require information on both the total

239   mass of paint used and the types of paint used. From our findings we can make recommendations

240   on the granularity of how many different types of paints should be tested for input into CTMs.

241   We recommend incorporating information on three categories of paints: 1) low-gloss, water-

242   based paints, 2) higher-gloss, water-based paints, and 3) oil-based paints.

243   The second major observation is that the distribution of IVOC versus VOC emissions

244   varies by paint type. The emissions from the lower gloss, indoor paints are mostly VOCs while a

245   significant fraction of the emissions from the High Gloss (98%) and SemiExt (87%) are IVOCs.

246   Furthermore, as we show in more detail below, the IVOC emissions from the lower gloss, indoor

247   paints are small and fall below our detection limits after the first hour following paint

248   application. This implies that emissions from the lower-gloss, indoor paints have little impact on

249   outdoor I/VOC concentrations and SOA formation.

250   By contrast, the high IVOC content of High Gloss and SemiExt emissions indicates that

251   they have larger SOA formation potential. In addition, since the SemiExt paints are exterior

252   paints, this means that 100% of their I/VOC emissions are released into the outdoor environment

253   and therefore impact ambient I/VOC concentrations and SOA formation.

254   The Oil paints have a closer to even split between IVOC and VOC emissions (36% and

255   64% respectively). Total I/VOC emissions from oil paints are about a factor of 10 larger than

256   emissions for SemiExt, and the Oil paint has the largest emissions of IVOCs among the paints

257   tested here. Oil paints are primarily used outdoors due to their hard-wearing properties.

258   Therefore, oil paints may also contribute significantly to ambient SOA formation.

259   Figure 2b shows that the distribution of compound classes emitted by the different types

260   of paints varies. Alkanes are a major component of the detected High Gloss and SemiExt

261   emissions (42% of the total mass for each). The low-gloss, indoor, water-based paints (Satin,

262   SemiInt, and Flat) and oil-based paint emit a wider spectrum of compounds. A significant

263   portion of emissions from the oil-based paints (12%) are aromatics. Aromatics typically have

264   high SOA yields[48] and are likely to significantly contribute to the SOA formation potential from

265   paints. Other important compound classes that are emitted by the paints are alcohols, aldehydes,

266   and ketones.

267   Using the measured emission rates (µg/g) of I/VOCs as well as the usage of each of the

268   six types of paints we were able to determine the total I/VOC emissions per mass of paint used in

269   the U.S. (g/kg). We estimate emissions of 291 g total I/VOCs (TVOCs) per kg of paint applied.

270   This estimate is in good agreement with prior literature. For example, McDonald et al. estimated

271   200 – 600 g TVOCs per kg of paint.[14] This indicates that existing inventories may serve as an

272   adequate estimator of I/VOC emissions from paints when laboratory tests are not feasible.

273   **3.2 Time evolution of emissions**
274
275   One potential characteristic of VCP emissions is that they can serve as long-term, low-

276   level emissions sources.[15,49] Our extended emissions experiments examine how paint emissions

277   evolved over time. Figure 3 shows how the fraction of emissions changed over the course of

278   multiple days as measured by the PTR-MS (mostly VOCs) and Tenax tubes (mostly IVOCs).
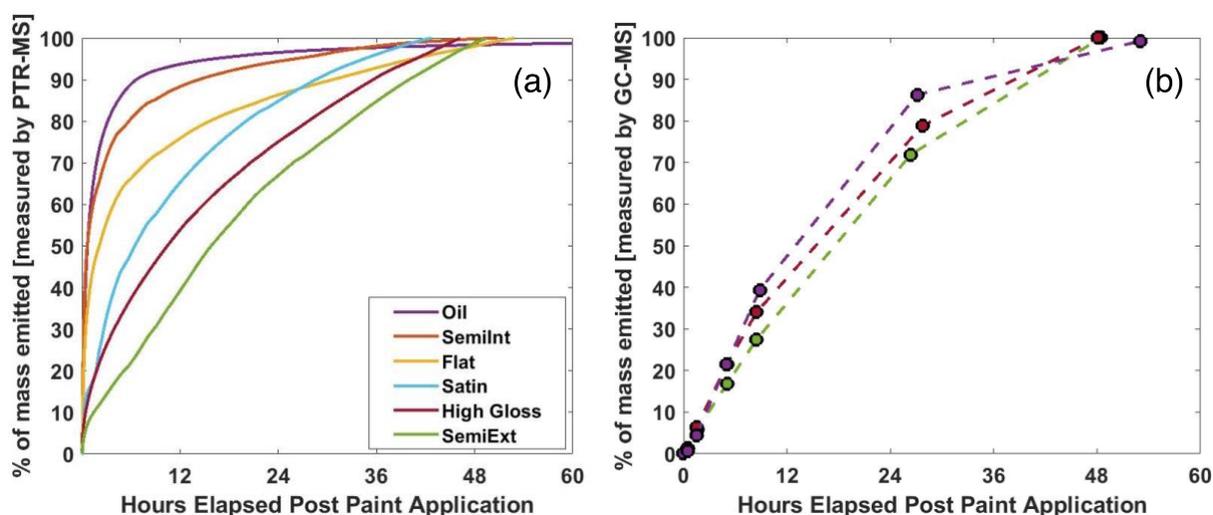
279

Figure 3. *Cumulative emissions measured by the (a) PTR-MS and (b) Tenax tubes as function of time elapsed after paint application. The colors of the legend apply to both panels. For these experiments, the PTR-MS operated*

continuously with ~2-minute time resolution. Dashed lines in (b) are to guide the eye between the periodic Tenax samples.

280

281   Figure 2 shows that the emissions from the indoor paints (Flat, Satin, SemiInt) as well as

282   the Oil paint were primarily VOCs. Figure 3 shows that the emissions from these paints fall off

283   rapidly. All four of these paints emit more than 50% of their total detected emissions within 12

284   hours after application. The temporal profile is most extreme for the Oil and SemiInt paints,

285   which emit >90% and >80% of their emissions within 12 hours, respectively. For low-gloss,

286   indoor paints there are no long term I/VOC emissions. Measurements of IVOCs using Tenax

287   tubes were below detection limits after one hour following paint application; the 0-1 hr tubes

288   were above detection limit, but the 1-2 hour and subsequent tubes were below detection.

289   The extended emissions experiments were run for more than two days for the Oil paint.

290   During preliminary tests, the Oil paint showed significantly larger I/VOC emissions compared to

291   the water-based paints. Therefore, a longer, one week (rather than two day) extended emissions

292   experiment was conducted for the Oil paint. IVOC emissions from the Oil paint fell below limits

293   of quantitation by the second day indicating a lack of long term IVOC emissions. The majority

294   of ions detected by the PTR-MS fell to background concentrations within the two-day drying

295   period. A list of ions that were still at concentrations greater than background levels after 48

296   hours of drying are included in Table S6.

297   While the total emissions from the Oil paint fall off rapidly, the emissions transition from

298   being VOC-dominated to IVOC-dominated over time. In general, the IVOCs are emitted more

299   slowly than the VOCs, as would be expected based on volatility. Figure 3b and Figure 4b show

300   that IVOC emissions from the oil paint persist for approximately one day after application.

301   Emissions from the SemiExt and High Gloss paints are dominated by IVOCs. Overall,

302   these paints emit more slowly compared to the other paints tested here. Figure 3a shows that

303   after 12 hours these paints emitted <50% of the total emissions detected by the PTR-MS. Most of

304   these emissions are IVOCs (e.g., naphthalene). For these paints all but two ions measured by the

305   PTR-MS reached background levels by the end of the two-day extended emissions experiment

306   (Table S6) but there were still IVOC emissions measured by the GC-MS at the end of the two-

307   day experiment.

308
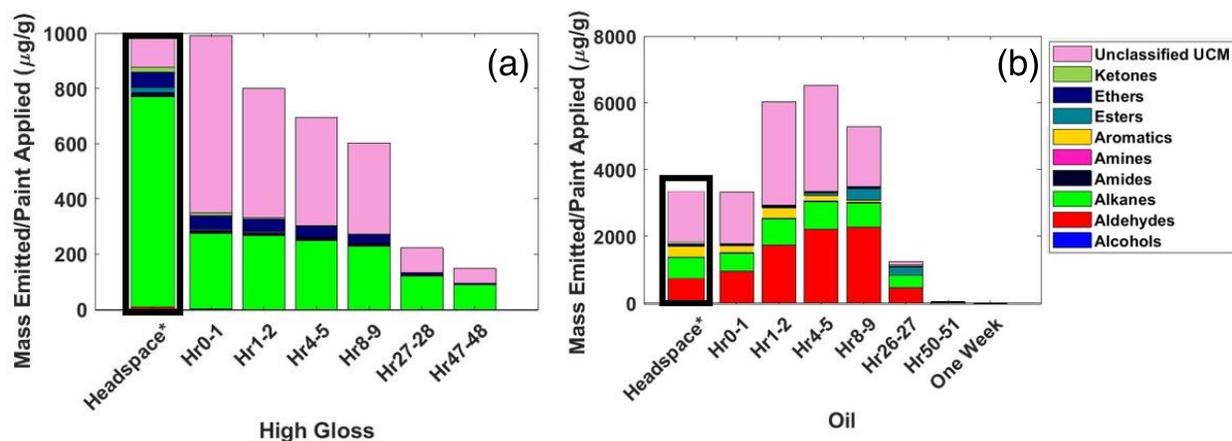
Figure 4. *Headspace and extended emission samples of (a) High Gloss and (b) Oil paints measured with Tenax tubes. The total height of the headspace samples is matched to the emission rate for the Hour 0-1 samples to aid comparison.*

309

310   Figure 4 shows the temporal evolution of IVOC emissions for the Oil and High Gloss

311   paints. IVOC emissions from the High Gloss gradually and continually decline over the course

312   of two days. However, even after 48 hours, the High Gloss paint continued to emit IVOCs at a

313   rate of 15% of the original rate during hour 0-1. The paints with low IVOC emissions (Flat,

314   SemiInt, Satin) had a similar profile of declining IVOC emissions with time, with emissions

315   falling below the detection limit within 1-2 hours after paint application. This suggests that some

316   paints can act as extended sources of IVOC emissions.

317   The composition of IVOC emissions changed over time. For example, for the high gloss

318   paint, alkanes were an important component of the emissions over the entire two days, but they

319   increased from 28% of the emitted mass during hour 0-1 to 60% at hour 47-48.

15

320   The evolution of IVOC emissions from the Oil paint was different. Emissions increased

321   relative to the hour 0-1 sample for hours 1-2, 4-5, and 8-9, before falling rapidly and eventually

322   reaching zero. As with the High Gloss, the composition of the IVOC emissions from the oil paint

323   also changed over time, with increasing aldehyde and ester fractions contributing to the higher

324   emissions at hours 1-2, 4-5, and 8-9.

325   **3.3 Headspace samples as representative emissions fingerprints**

326
327   One question our data can address is whether the headspace samples can serve as a

328   fingerprint for the I/VOC emissions of paints. Figure S4 clearly shows that this is not possible

329   for VOCs. Figure S4 shows the PTR-MS measurements of VOCs from both a headspace sample

330   and an extended emission sample of High Gloss paint. The headspace sample is dominated by

331   acetone (*m/z* 59) and methanol (*m/z* 33). In the extended emissions tests methanol and acetone

332   contributed less than 10% of the total VOC emissions.

333   Similarly, the GC-MS measurements also demonstrate that a headspace sample does not

334   capture the total emissions profile of a paint over time. Figure 4 shows the headspace

335   composition of the Oil and High Gloss paints next to the emission composition over the drying

336   period. The High Gloss headspace sample is enhanced in alkanes relative to the extended

337   emissions samples. The Oil headspace composition is similar to the emissions within the first

338   hour following the application of the oil paint. However, as the oil paint dries the composition of

339   the emissions changes. Aldehydes become a more important part of the emissions for the 1-2, 4-

340   5, and 8-9 hour samples. Low volatility esters are also emitted, but only after 8 hours following

341   paint application. If headspace samples were used as an emission fingerprint these less-volatile

342   emissions would be underestimated.

343

3.4 Implications for SOA formation

Here we combine our new emissions data with literature SOA yields to estimate total I/VOC emissions from paints in the U.S. and potential impacts on SOA formation. We used the U.S. Economic Census to scale our measured I/VOC emission factors to a national scale.[33] We mapped the US Economic Census' 23 different subcategories of "Architectural Coatings" to one of our six paint types tested. Since the census reported paint usage for 2010 the usage was scaled by population growth to obtain estimated paint usage for 2021. The mass of paints used for each of the six classes tested were multiplied by the measured I/VOC emission factors to estimate the total expected I/VOC emissions from paints in the U.S. These total I/VOC emissions were then multiplied by SOA yields to determine projected SOA formation.

Figure 5a and Table 1 summarize the paint usage. Flat, SemiInt, SemiExt, and Oil paints each contribute ~20-30% (~600-900 Gg) of annual paint usage in the U.S. Satin and High Gloss each contribute less than 10% of total paint usage. We estimate total paint I/VOC emissions of ~169 Gg/year. Most of these emissions (59%, Figure 5c) are VOCs, with the remainder being IVOCs.

Total I/VOCs emissions from paints are high on a mass of product used basis. Emissions are approximately 290 g I/VOC per kg of paint used. This corresponds to 0.51 kg/person of I/VOCs emitted per year in the US. This is one to two orders of magnitude greater than the I/VOC emission rates of gasoline and diesel related emissions (on a gram of I/VOC per kg of fuel used basis).[14] Our per-person and per mass estimates of paint I/VOC emissions are similar to recent estimates by McDonald et al (200 - 600 g/kg of product)[14] and Seltzer et al (0.67 kg/person per year).[20]
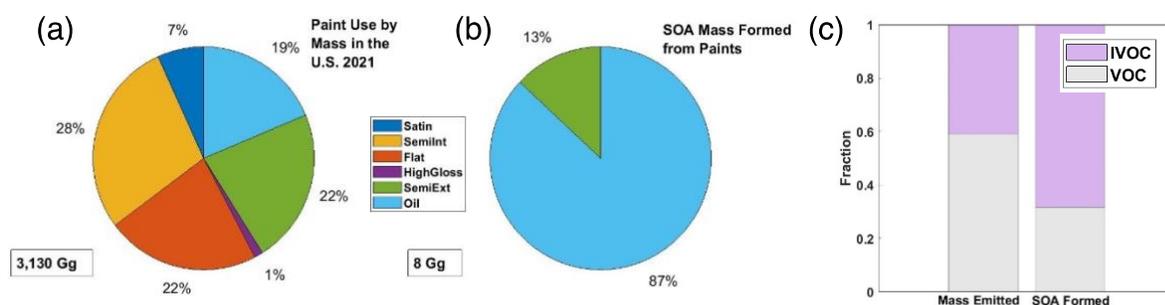
Figure 5. *(a) Total paint usage in the U.S. reported by U.S. Census Bureau (b) SOA mass formed, and (c) contributions of I/VOCs to paint emissions and SOA formation. The split between paint use by mass is fairly evenly divided between SemiInt, Flat, SemiExt, and Oil based paints. SOA mass is dominated by I/VOC emissions from Oil and SemiExt paints. The IVOCs are more important than VOCs for SOA formation.*

Table 1 Paint usage and emissions. *Total paint usage in the U.S. for each paint type, the total I/VOC yearly emissions in the U.S. for each paint type, and the SOA mass formed each year in the U.S. by paints. Uncertainty in I/VOC emissions is based on precision in replicate experiments. Uncertainty in SOA production is based on uncertainty in reported SOA yields.*

Paint Type	Paint Usage in US 2021 [Gg]	IVOC+VOC Emissions [Gg]	SOA Mass Formed [Mg]
Oil	584	152.6 [+/- 13.7]	6,947 [+/- 640.5]
Semi-Gloss Interior (SemiInt)	892	0.09 [+/- .008]	2.1 [+/- 0.19]
Flat	702	0.06 [+/- .005]	1.5 [+/- 0.14]
Satin	212	0.04 [+/- .004]	0.9 [+/- 0.08]
Semi-Gloss Exterior (SemiExt)	701	15.9 [+/- 1.4]	1,042 [+/- 96.1]
High Gloss	39	0.3 [+/- .03]	18.7 [+/- 1.72]

While usage is somewhat evenly distributed across several paint types, I/VOC emissions are dominated by two classes: Oil and SemiExt. These two classes have the highest emission factors (µg/g) shown in Figure 2, and together they contribute 98% of total emissions. In particular, oil paints account for 90% of total paint I/VOC emissions.

We estimated the contribution of paint emitted I/VOCs to ambient SOA production. We estimated SOA production by multiplying the total I/VOC emissions by SOA mass yields for

380   each compound class. The SOA yields (g/g) were calculated using the Statistical Oxidation

381   Model (SOM)[50] and are shown in Table S7.

382   We estimate annual SOA production of ~8 Gg from paint I/VOCs (Table 1) and an

383   overall SOA mass yield of 4.7% [+/- 2%]. Figure 5 and Table 1 show that SOA production is

384   dominated by Oil and SemiExt paints. The other four paint types contribute negligibly to

385   predicted SOA formation due to their comparatively low emissions. IVOCs account for 68% of

386   predicted SOA formation, underscoring the importance of lower volatility and high SOA yield

387   precursors.

388   To put the SOA production from paints in context, we compare to estimates of SOA

389   formation from vehicle emissions. Jathar et al. estimated that on-road gasoline and diesel vehicle

390   emissions generate ~120 Gg of SOA annually in the U.S.[16] Our estimate of 8 Gg of SOA from

391   paints is about 6.7% of the amount of vehicle-generated SOA. However, paints are just one

392   subcategory of a subcategory (architectural coatings) of the entire VCP sector. Thus, these

393   calculations highlight how important it is to understand SOA formation from the entire VCP

394   sector especially as on-road sources become cleaner and emit less SOA precursors.

395   There are several potential sources of uncertainty in our estimates of paint I/VOC

396   emissions and subsequent SOA formation. These include uncertainty in SOA yields, especially

397   for UCM and oxygenated VOCs that have not been directly measured in the laboratory. There

398   may be significant variation in paint emissions rate and composition across manufacturers that

399   we did not capture here. Since our results suggest that emissions and SOA formation are

400   dominated by paints that are often used outdoors, the role of sunlight-driven changes in

401   emissions[51] should be considered in future studies.

In this study, we have been able to reduce one potential source of uncertainty in the contribution of paint I/VOCs to ambient SOA. The four paint types that are often used indoors (Satin, SemiInt, Flat, and High Gloss) all had low emissions and negligible SOA contributions. One potential confounder for the ambient impact of these emissions is indoor-to-outdoor transit (i.e., paint fumes need to leave the building without being lost to walls or other surfaces). Our data suggest that these indoor paints are a minor contributor to I/VOC emissions from the paints and coatings sector, and that emissions and SOA formation are dominated by paints used outdoors.

References

(1)   Di, Q.; Wang, Y.; Zanobetti, A.; Wang, Y.; Koutrakis, P.; Choirat, C.; Dominici, F.; Schwartz, J. D. Air Pollution and Mortality in the Medicare Population. *N. Engl. J. Med.* **2017**, *376* (26), 2513–2522.

(2)   Dockery, D. W.; Pope III, C. A.; Xu, X.; al., et. An Association between Air Pollution and Mortality in Six U.S. Cities. *N. Engl. J. Med.* **1993**, *329*, 1753–1759.

(3)   Gakidou, E.; Afshin, A.; Abajobir, A. A.; Abate, K. H.; Abbafati, C.; Abbas, K. M.; Abd-Allah, F.; Abdulle, A. M.; Abera, S. F.; Aboyans, V.; et al. Global, Regional, and National Comparative Risk Assessment of 84 Behavioural, Environmental and Occupational, and Metabolic Risks or Clusters of Risks, 1990–2016: A Systematic Analysis for the Global Burden of Disease Study 2016. *Lancet* **2017**, *390* (10100), 1345–1422.

(4)   Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Allan, J. D.; Coe, H.; Ulbrich, I.; Alfarra, M. R.; Takami, A.; Middlebrook, A. M.; Sun, Y. L.; et al. Ubiquity and Dominance of Oxygenated Species in Organic Aerosols in Anthropogenically-Influenced Northern Hemisphere Midlatitudes. *Geophys. Res. Lett.* **2007**, *34*, L13801.

(5)   Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging. *Science (80-.).* **2007**, *315*, 1259–1262.

(6)   Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L. T.; Worsnop, D. R.; Molina, M. J. Secondary Organic Aerosol Formation from Anthropogenic Air Pollution: Rapid and Higher than Expected. *Geophys. Res. Lett.* **2006**, *33*, L17811.

(7)   Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; et al. Evolution of Organic Aerosols in the Atmosphere. *Science (80-.).* **2009**, *326* (5959), 1525–1529.

(8)   Xu, L.; Suresh, S.; Guo, H.; Weber, R. J.; Ng, N. L. Aerosol Characterization over the Southeastern United States Using High-Resolution Aerosol Mass Spectrometry: Spatial and Seasonal Variation of Aerosol Composition and Sources with a Focus on Organic Nitrates. *Atmos. Chem. Phys.* **2015**, *15* (13), 7307–7336.

(9) Chan, A. W. H.; Kautzman, K. E.; Chhabra, P. S.; Surratt, J. D.; Chan, M. N.; Crounse, J. D.; Kurten, A.; Wennberg, P. O.; Flagan, R. C.; Seinfeld, J. H. Secondary Organic Aerosol Formation from Photooxidation of Naphthalene and Alkylnaphthalenes: Implications for Oxidation of Intermediate Volatility Organic Compounds (IVOCs). *Atmos. Chem. Phys.* **2009**, *9* (9), 3049–3060.

(10) Miracolo, M. A.; Presto, A. A.; Lambe, A. T.; Hennigan, C. J.; Donahue, N. M.; Kroll, J. H.; Worsnop, D. R.; Robinson, A. L. Secondary Organic Aerosol Formation from Low-Volatility Organic Vapors in Motor Vehicle Emissions. *Environ. Sci. Technol.* **2010**, *44* (5), 1638–1643.

(11) Presto, A. A.; Miracolo, M. A.; Donahue, N. M.; Robinson, A. L. Secondary Organic Aerosol Formation from High-NOx Photo-Oxidation of Low Volatility Precursors: N-Alkanes. *Environ. Sci. Technol.* **2010**, *44* (6), 2029–2034.

(12) Zhao, Y.; Hennigan, C. J.; May, A. A.; Tkacik, D. S.; de Gouw, J. A.; Gilman, J. B.; Kuster, W. C.; Borbon, A.; Robinson, A. L. Intermediate-Volatility Organic Compounds: A Large Source of Secondary Organic Aerosol. *Environ. Sci. Technol.* **2014**, *48*, 13743–13750.

(13) Bishop, G. A.; Haugen, M. J. The Story of Ever Diminishing Vehicle Tailpipe Emissions as Observed in the Chicago, Illinois Area. *Environ. Sci. Technol.* **2018**, *52* (13), 7587–7593.

(14) McDonald, B. C.; de Gouw, J. A.; Gilman, J. B.; Jathar, S. H.; Akherati, A.; Cappa, C. D.; Jimenez, J. L.; Lee-Taylor, J.; Hayes, P. L.; McKeen, S. A.; et al. Volatile Chemical Products Emerging as Largest Petrochemical Source of Urban Organic Emissions. *Science (80-.).* **2018**, *359* (6377), 760.

(15) Khare, P.; Gentner, D. R. Considering the Future of Anthropogenic Gas-Phase Organic Compound Emissions and the Increasing Influence of Non-Combustion Sources on Urban Air Quality. *Atmos. Chem. Phys* **2018**, *185194*, 5391–5413.

(16) Jathar, S. H.; Gordon, T. D.; Hennigan, C. J.; Pye, H. O. T.; Pouliot, G.; Adams, P. J.; Donahue, N. M.; Robinson, A. L. Unspeciated Organic Emissions from Combustion Sources and Their Influence on the Secondary Organic Aerosol Budget in the United States. *Proc. Nat. Acad. Sci.* **2014**, *111*, 10473–10478.

(17) Hodzic, A.; Jimenez, J. L.; Madronich, S.; Canagaratna, M. R.; DeCarlo, P. F.; Kleinman, L.; Fast, J. Modeling Organic Aerosols in a Megacity: Potential Contribution of Semi-Volatile and Intermediate Volatility Primary Organic Compounds to Secondary Organic Aerosol Formation. *Atmos. Chem. Phys.* **2010**, *10*, 5491–5514.

(18) Murphy, B. N.; Woody, M. C.; Jimenez, J. L.; Marie, A.; Carlton, G.; Hayes, P. L.; Liu, S.; Ng, N. L.; Russell, L. M.; Setyan, A.; et al. Semivolatile POA and Parameterized Total Combustion SOA in CMAQv5.2: Impacts on Source Strength and Partitioning. *Atmos. Chem. Phys* **2017**, *175194*, 11107–11133.

(19) Shah, R. U.; Coggon, M. M.; Gkatzelis, G. I.; McDonald, B. C.; Tasoglou, A.; Huber, H.; Gilman, J.; Warneke, C.; Robinson, A. L.; Presto, A. A. Urban Oxidation Flow Reactor Measurements Reveal Significant Secondary Organic Aerosol Contributions from Volatile Emissions of Emerging Importance. *Environ. Sci. Technol.* **2020**, *54* (2).

(20) Seltzer, K. M.; Pennington, E.; Rao, V.; N. Murphy, B.; Strum, M.; K. Isaacs, K.; O. T. Pye, H. Reactive Organic Carbon Emissions from Volatile Chemical Products. *Atmos. Chem. Phys.* **2021**, *21* (6), 5079–5100.

(21) Guo, Z.; Chang, J. C. S.; Sparks, L. E.; Fortmann, R. C. Estimation of the Rate of VOC

486   Emissions from Solvent-Based Indoor Coating Materials Based on Product Formulation.
487   *Atmos. Environ.* **1999**, *33* (8), 1205–1215.

488 (22)   Kiil, S. Drying of Latex Films and Coatings: Reconsidering the Fundamental
489   Mechanisms. *Prog. Org. Coatings* **2006**, *57* (3), 236–250.

490 (23)   Stockwell, C. E.; Coggon, M. M.; I. Gkatzelis, G.; Ortega, J.; McDonald, B. C.; Peischl,
491   J.; Aikin, K.; Gilman, J. B.; Trainer, M.; Warneke, C. Volatile Organic Compound
492   Emissions from Solvent-and Water-Borne Coatings-Compositional Differences and
493   Tracer Compound Identifications. *Atmos. Chem. Phys.* **2021**, *21* (8), 6005–6022.

494 (24)   Zhao, P.; Cheng, Y.-H.; Lin, C.-C.; Cheng, Y.-L. Effect of Resin Content and Substrate on
495   the Emission of BTEX and Carbonyls from Low-VOC Water-Based Wall Paint. *Environ.*
496   *Sci. Pollut. Res.* **2016**, *12*, 3799–3808.

497 (25)   Silva, G. V.; Teresa, M.; Vasconcelos, S. D.; Santos, A. M.; Fernandes, E. O. Comparison
498   of the Substrate Effect on VOC Emissions from Water Based Varnish and Latex Paint.
499   *Environ. Sci. Pollut. Res.* **2003**, *10* (4), 209–216.

500 (26)   Chang, J. C. S.; Tichenor, B. A.; Guo, Z.; Krebs, K. A. Substrate Effects on VOC
501   Emissions from a Latex Paint. *Indoor Air* **1997**, *7* (4), 241–247.

502 (27)   Clausen, P. A.; Wolkoff, P.; Hoist, E.; Nielsen, P. A. Long-Term Emission of Volatile
503   Organic Compounds from Waterborne Paints – Methods of Comparison. *Indoor Air* **1991**,
504   *1* (4), 562–576.

505 (28)   Lin, C.-C.; Corsi, R. L. Texanol Ester Alcohol Emissions from Latex Paints: Temporal
506   Variations and Multi-Component Recoveries. *Atmos. Environ.* **2007**, *41*, 3225–3234.

507 (29)   CORSI, R. L.; LIN, C.-C. Emissions of 2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate
508   (TMPD-MIB) from Latex Paint: A Critical Review. *Crit. Rev. Environ. Sci. Technol.*
509   **2009**, *39* (12), 1052–1080.

510 (30)   Gandolfo, A.; Marque, S.; Temime-Roussel, B.; Gemayel, R.; Wortham, H.; Truffier-
511   Boutry, D.; Bartolomei, V.; Gligorovski, S. Unexpectedly High Levels of Organic
512   Compounds Released by Indoor Photocatalytic Paints. *Environ. Sci. Technol.* **2018**, *52*
513   (19), 11328–11337.

514 (31)   Fortmann, R.; Roache, N.; Chang, J. C. S.; Guo, Z. Characterization of Emissions of
515   Volatile Organic Compounds from Interior Alkyd Paint.
516   *https://doi.org/10.1080/10473289.1998.10463741* **2011**, *48* (10), 931–940.

517 (32)   Goliff, W. S.; Fitz, D. R.; Cocker, K.; Bumiller, K.; Bufalino, C.; Switzer, D. Ambient
518   Measurements of 2,2,4-Trimethyl, 1,3-Pentanediol Monoisobutyrate in Southern
519   California. *http://dx.doi.org/10.1080/10962247.2012.666223* **2012**, *62* (6), 680–685.

520 (33)   Bureau, U. C. *2012 Economic Census Survey, Manufacturing Industry Series: Materials*
521   *Consumed by Kind for the U.S*; 2012.

522 (34)   Weiss, K. D. Paint and Coatings: A Mature Industry in Transition. *Prog. Polym. Sci.* **1997**,
523   *22* (2), 203–245.

524 (35)   EPA, U. S. *National Volatile Organic Compound Emission Standards for Architectural*
525   *Coatings*; 2000; p 40 CFR Part 59 Subpart D.

526 (36)   Lindinger, W.; Hansel, A.; Jordan, A. On-Line Monitoring of Volatile Organic
527   Compounds at Pptv Levels by Means of Proton-Transfer-Reaction Mass Spectrometry
528   (PTR-MS) Medical Applications, Food Control and Environmental Research. *Int. J. Mass*
529   *Spectrom. Ion Process.* **1998**, *173* (3), 191–241.

530 (37)   Helmig, D.; Vierling, L. Water Adsorption Capacity of the Solid Adsorbents Tenax TA,
531   Tenax GR, Carbotrap, Carbotrap C, Carbosieve SIII, and Carboxen 569 and Water

Management Techniques for the Atmospheric Sampling of Volatile Organic Trace Gases. *Anal. Chem.* **2002**, *67* (23), 4380–4386.

(38) Maier, I.; Fieber, M. Retention Characteristics of Volatile Compounds on Tenax TA. *J. High Resolut. Chromatogr.* **1988**, *11* (8), 566–576.

(39) Rothweiler, H.; Wäger, P. A.; Schlatter, C. Comparison of Tenax Ta and Carbotrap for Sampling and Analysis of Volatile Organic Compounds in Air. *Atmos. Environ. Part B. Urban Atmos.* **1991**, *25* (2), 231–235.

(40) Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L. Intermediate Volatility Organic Compound Emissions from On-Road Gasoline Vehicles and Small Off-Road Gasoline Engines. *Environ. Sci. Technol.* **2016**, *50* (8), 4554–4563.

(41) Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L. Intermediate Volatility Organic Compound Emissions from On-Road Diesel Vehicles: Chemical Composition, Emission Factors, and Estimated Secondary Organic Aerosol Production. *Environ. Sci. Technol.* **2015**, *49* (19), 11516–11526.

(42) Presto, A. A.; Hennigan, C. J.; Nguyen, N. T.; Robinson, A. L. Determination of Volatility Distributions of Primary Organic Aerosol Emissions from Internal Combustion Engines Using Thermal Desorption Gas Chromatography Mass Spectrometry. *Aerosol Sci. Technol.* **2012**, *46* (10), 1129–1139.

(43) Xu, R.; Alam, M. S.; Stark, C.; Harrison, R. M. Behaviour of Traffic Emitted Semi-Volatile and Intermediate Volatility Organic Compounds within the Urban Atmosphere. *Sci. Total Environ.* **2020**, *720*, 137470.

(44) Lu, Q.; Zhao, Y.; Robinson, A. L. Comprehensive Organic Emission Profiles for Gasoline, Diesel, and Gas-Turbine Engines Including Intermediate and Semi-Volatile Organic Compound Emissions. *Atmos. Chem. Phys.* **2018**, *18*, 17637–17654.

(45) Pankow, J. F.; Asher, W. E. SIMPOL.1: A Simple Group Contribution Method for Predicting Vapor Pressures and Enthalpies of Vaporization of Multifunctional Organic Compounds. *Atmos. Chem. Phys.* **2008**, *8* (10), 2773–2796.

(46) McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra*, 4th Editio.; University Science Books, 1993.

(47) Pagonis, D.; Sekimoto, K.; de Gouw, J. A Library of Proton-Transfer Reactions of H3O+ Ions Used for Trace Gas Detection. *J. Am. Soc. Mass Spectrom.* **2019**, *30* (7), 1330–1335.

(48) Akherati, A.; He, Y.; Coggon, M. M.; Koss, A.; Hodshire, A.; Sekimoto, K.; Warneke, C.; de Gouw, J. A.; Yee, L. D.; Seinfeld, J. H.; et al. Oxygenated Aromatic Compounds Are Important Precursors of Secondary Organic Aerosol in Biomass Burning Emissions. *Environ. Sci. Technol.* **2020**, *54*, 8579.

(49) Drozd, G. T.; Weber, R. J.; Goldstein, A. H. Highly Resolved Composition during Diesel Evaporation with Modeled Ozone and Secondary Aerosol Formation: Insights into Pollutant Formation from Evaporative Intermediate Volatility Organic Compound Sources. *Environ. Sci. Technol.* **2021**, *55* (9), 5742–5751.

(50) Cappa, C. D.; Wilson, K. R. Multi-Generation Gas-Phase Oxidation, Equilibrium Partitioning, and the Formation and Evolution of Secondary Organic Aerosol. *Atmos. Chem. Phys.* **2012**, *12*, 9505–9528.

(51) Khare, P.; Machesky, J.; Soto, R.; He, M.; Presto, A. A.; Gentner, D. R. Asphalt-Related Emissions Are a Major Missing Nontraditional Source of Secondary Organic Aerosol Precursors. *Sci. Adv.* **2020**, *6* (36), eabb9785.

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Supporting Information

580 Supporting information is available free of charge. Additional description of experimental
581 procedures and two figures showing experimental setups; a table outlining specific experiments
582 and sampling times; tables with lists of ion identification in the PTR-MS and marker ions used in
583 the GC-MS; SOA yields used in the calculation of SOA formation potential; figures showing
584 headspace samples for all paint types and the difference in VOCs measured in headspace and
585 extended emissions experiments.

586

Acknowledgments

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Data Availability

591 Experimental data are available on the KiltHub repository at
592 https://doi.org/10.1184/R1/14814813.v1