



1 Volatile organic compound emissions from solvent- and water- 2 borne coatings: compositional differences and tracer compound 3 identifications

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5 Chelsea E. Stockwell^{1,2}, Matthew M. Coggon^{1,2}, Georgios I. Gkatzelis^{1,2,a}, John Ortega^{1,2}, Brian
6 C. McDonald¹, Jeff Peischl^{1,2}, Kenneth Aikin^{1,2}, Jessica B. Gilman¹, Michael Trainer¹, Carsten
7 Warneke^{1,2}

8 ¹NOAA, Chemical Sciences Laboratory, Boulder, Colorado 80305, United States

9 ²Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado 80309,
10 United States

11 ^anow at: Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich,
12 Germany

13 **Correspondence:** Chelsea Stockwell (chelsea.stockwell@noaa.gov) and Carsten Warneke
14 (carsten.warneke@noaa.gov)
15

16 **Abstract.** The emissions of volatile organic compounds (VOCs) from volatile chemical products (VCPs) - specifically
17 personal care products, cleaning agents, coatings, adhesives, and pesticides - are emerging as the largest source of
18 petroleum-derived organic carbon in US cities. Previous work has shown that the ambient concentration of markers
19 for most VCP categories correlate strongly with population density except for VOCs predominantly originating from
20 solvent- and water-borne coatings (e.g., parachlorobenzotrifluoride (PCBTF) and Texanol®, respectively). Instead,
21 these enhancements were dominated by distinct emission events likely driven by industrial usage patterns, such as
22 construction activity. In this work, the headspace of a variety of coating products was analyzed using a proton-transfer-
23 reaction time-of-flight mass spectrometer (PTR-ToF-MS) and a gas chromatography (GC) pre-separation front-end to
24 identify composition differences for various coating types (e.g., paints, primers, sealers and stains). Evaporation
25 experiments of several products showed high initial VOC emission rates and for the length of these experiments, the
26 majority of the VOC mass was emitted during the first few hours following application. The percentage of mass
27 emitted as measured VOCs (< 1 to 83%) mirrored the VOC content reported by the manufacturer (<5 to 550 g L⁻¹).
28 Ambient and laboratory measurements, usage trends, and ingredients compiled from architectural coatings surveys
29 show both PCBTF and Texanol account for ~10% of the total VOC ingredient sales and therefore can be useful tracers
30 for solvent- and water-borne coatings.
31

32 1 Introduction

33 After decades of declining mixing ratios of volatile organic compounds (VOCs) in urban areas (Warneke et al., 2012),
34 volatile chemical products (VCPs = coatings, adhesives, inks, personal care products, and cleaning agents) have
35 emerged as a major source of petrochemical organics in the urban atmosphere (McDonald et al., 2018a). Measurement
36 and modeling efforts have already shown that VCP emissions and their contribution to urban ozone formation are
37 comparable to those for fossil fuel VOCs in Los Angeles and other cities in the United States (McDonald et al., 2018a;



38 Coggon et al., 2020). Reductions in tailpipe emissions of VOCs from gasoline vehicles are slowing, and diminishing
39 returns from emission control technologies have been reported for on-road vehicles (Bishop and Haugen, 2018). With
40 slowing trends in ozone precursors and shifts in ozone production regimes, decreases in ozone design values may have
41 slowed as well (Parrish et al., 2017).

42 A fuel-based inventory by McDonald et al. (2018a) showed that about 18% of the petrochemical VOC
43 emissions in Los Angeles in 2010 were from personal care products. Coggon et al. (2018) found that D5 siloxane,
44 which is a unique tracer for personal care product emissions, is emitted in urban areas in similar amounts as benzene
45 from vehicles, indicating a significant emission source of personal care products. The next largest emission source
46 was from coatings accounting for approximately 13% of the VOC inventory in Los Angeles. Coatings in emission
47 inventories are defined as paints, varnishes, primers, stains, sealers, lacquers, and other solvents associated with
48 coatings (e.g., thinners, cleaners, additives). This includes both industrial and architectural uses, which comprise half-
49 and-half of the coating fraction. The impact of VOC emissions from coatings has been investigated in the indoor
50 environment (Corsi and Lin, 2009; Weschler and Nazaroff, 2012; Schieweck and Bock, 2015; Kozicki et al., 2018),
51 but few measurements have been reported in the outdoor environment. Urban air is likely impacted from coating
52 emissions from indoor/outdoor exchange as well as from architectural and industrial coating usage outdoors. To
53 quantify VCP coating emissions in urban air, it is important to identify VOC tracers that are uniquely linked to water-
54 and solvent-borne usage, analogous to the emissions of D5 siloxane from personal care products. Although there is a
55 lack of detailed analysis of coatings emissions in the ambient atmosphere, emissions suspected from coatings have
56 been measured in ambient air. Goliff et al. (2012) measured 2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (TPM,
57 also known as Texanol®), a common solvent in water-borne coatings, in Southern California at mixing ratios of up to
58 20 ppt with the largest values in summer, when coating activities are typically the highest.

59 The composition and emissions of chemical products have changed significantly in recent decades in an
60 effort to reduce the ozone (O₃) and secondary organic aerosol (SOA) formation potential (Weschler, 2009; CARB,
61 2015; Shin et al., 2016). For example, water-borne paints are increasingly replacing solvent-borne paints, while
62 simultaneously many VOC ingredients are being replaced with water (Matheson, 2002), “exempt” VOCs, or low-
63 vapor-pressure VOCs (LVP-VOCs) (Li et al., 2018). The California Air Resources Board (CARB) defines “exempt”
64 VOCs as compounds that are not expected to meaningfully contribute to ozone formation due to their low reactivity
65 in the atmosphere. Examples include acetone, ethane, perchloroethylene, methyl acetate, and
66 parachlorobenzotrifluoride (PCBTF). CARB also exempts several LVP-VOC, which are defined as chemical
67 compounds containing at least one carbon atom and a vapor pressure less than 0.1 mm Hg at 20°C, organic compounds
68 with more than 12 carbon atoms, compounds with boiling points greater than 216°C, chemical mixtures comprised
69 solely of compounds with more than 12 carbon atoms, or as the weight percent of a chemical mixture that boils above
70 216°C (Li et al., 2018). As a result of product reformulations and VOC exemptions, many paints can now be classified
71 as “zero VOC” paints that fall below the government-regulated permissible amounts, even though they emit
72 compounds that are more broadly defined within the category of VOC.

73 Presented here are ambient and laboratory measurements of vapors emitted from coatings using a proton-
74 transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS). Ambient measurements show the spatial and



75 temporal trends of PCBTF and Texanol emissions in New York City (NYC), Chicago, Pittsburgh, and Denver. These
76 ambient measurements are linked to coatings using a series of laboratory measurements sampling various architectural
77 coatings. First, we compare VOC composition from coating headspace samples analyzed using PTR-ToF-MS with
78 gas chromatograph (GC) pre-separation. These measurements highlight the differences in VOC composition for a
79 variety of coating products and help to unambiguously identify VOC tracers linked to solvent and water-borne
80 coatings. Emission factors (g kg^{-1}) of VOC mass are measured via controlled evaporation experiments to quantify key
81 VOC emissions from coating use. Lastly, ingredient compilations from architectural coatings surveys from CARB are
82 compared with the laboratory measurements to confirm usage trends. Coating surveys generally agree with the
83 ambient and laboratory measurements and support the assignment of Texanol and PCBTF as atmospheric tracers for
84 water-borne and solvent-borne coatings.

85

86 **2 Experimental Methods**

87

88 **2.1. Instrumentation**

89 **2.1.1 PTR-ToF-MS**

90 Mixing ratios of VOCs in ambient and laboratory measurements were determined using a proton-transfer-reaction
91 time-of-flight mass spectrometer (PTR-ToF-MS; referred to hereafter as PTR-ToF) (Yuan et al., 2016; Yuan et al.,
92 2017). The PTR-ToF measures a large range of aromatics, alkenes, nitrogen-containing species, and oxygenated
93 VOCs. Instrument backgrounds were determined for laboratory measurements before and after every experiment for
94 short duration experiments, or every 2 h for longer duration experiments and ambient measurements, by passing air
95 through a platinum catalyst heated to 350°C. Data were processed following the recommendations of Stark et al.
96 (2015) using the Tofware package in Igor Pro (WaveMetrics). The PTR-ToF was calibrated using gravimetrically-
97 prepared gas standards for typical water-borne solvents such as acetone and methyl ethyl ketone, and solvent-borne
98 compounds such as toluene and C8-aromatics. Texanol and PCBTF were calibrated by liquid calibration methods as
99 described by Coggon et al. (2018). The sensitivities for Texanol and PCBTF for 1 second measurements was 9 and
100 69 normalized counts per second per ppbv (ncps ppbv^{-1}), respectively, and the detection limits for both were < 10 pptv
101 (Gkatzelis et al. 2020a). The sensitivity of compounds that were not calibrated were calculated according to Sekimoto
102 et al. (2017).

103 The PTR-ToF is less sensitive to smaller hydrocarbons (de Gouw and Warneke, 2007; Sekimoto et al., 2017)
104 and substantially underestimates their mixing ratios. PTR-ToF sensitivities to alkanes and alkenes are typically only
105 a few percent of those for oxygenates (Warneke et al., 2003), and the sensitivities calculated using methods outlined
106 in (Sekimoto et al., 2017) are likely overestimated. Theoretical calibration factors from reaction rate coefficients have
107 been shown to be biased high for alkanes and alkenes (Warneke et al., 2003). In order to more accurately quantify the
108 contributions of hydrocarbons (HCs), the calculated sensitivities for low molecular weight HCs (< C5) were assumed
109 to have the same sensitivity as low molecular weight alkanes ($10 \text{ ncps ppbv}^{-1}$). This results in an estimated uncertainty
110 in total VOC emissions of about a factor of two.

111



112 2.1.2 GC Front End to PTR-ToF-MS

113

114 PTR-ToF-MS only resolves VOC molecular formulae. Gas chromatography (GC) pre-separation has been used
115 previously to identify structural isomers (Warneke et al., 2003; Koss et al., 2016). Here a custom-built GC described
116 by Kuster et al. (2004) was updated and re-designed specifically as a PTR-ToF-MS front end to analyze the complex
117 headspace mixture of select coating formulations. Details describing the setup and performance of the GC interface
118 are provided in the supplemental information and only a brief description is provided here.

119 The GC consists of a 30 m DB-624 column (Agilent Technologies, 30 m, 0.25 mm ID, 1.4 μm film thickness)
120 and oven combination identical to the system described by Lerner et al. (2017), a liquid nitrogen cryotrap, and a 2
121 position 10-port valve (VICI) to direct gas flows. The column was selected to measure polar and nonpolar VOCs in
122 the approximate range of C₄-C₁₀. The effluent of the GC column is injected into the PTR-ToF inlet. Depending on
123 the application, 1-5 minute samples can be collected and chromatogram lengths of 10-20 minutes can be chosen such
124 that the total run time is between 15 and 30 minutes. LabVIEW (National Instruments) software controls the sequence
125 of events, hot and cold trap temperatures, valve switching, sample flow and carrier gas flow. The detection limit for
126 commonly detected VOCs (e.g., isoprene, benzene, xylenes) using this cryofocusing system is ~ 5 pptv.

127

128 2.2. Laboratory Measurements

129 Laboratory measurements were performed to qualitatively evaluate the headspace VOCs emitted from commonly used
130 coatings. Nineteen different solvent- or water-borne formulas were tested, and ranged in applications including paints,
131 stains, primers, sealers, and preservatives. It is worth noting that industrial coatings formulated to withstand extreme
132 environmental conditions were not a part of this survey. The headspace VOCs were sampled by placing the product
133 container close to the PTR-ToF inlet and zero air was sampled between runs. The GC-front end was used to aid the
134 specific identification of VOC isomers emitted from different coating types, which were compared to the ingredient
135 lists or CARB coating surveys.

136 Several representative products were sampled over longer periods to investigate their evaporative behavior:
137 a solvent-borne polyurethane stain, a latex paint, a primer/sealer paint, and a “zero VOC” low odor paint. These
138 evaporation experiments were performed by flowing synthetic air (2 L min^{-1}) through a Teflon coated chamber
139 enclosing a microbalance scale (Ohaus) for a minimum of 19 hours. Prior to each experiment, the chamber was flushed
140 until background VOC concentration were < 50 ppt. Experiments were initialized by depositing small (< 50 mg)
141 samples of coating product through a septum and onto a small piece of Teflon plastic placed on the scale. The PTR-
142 ToF monitored VOCs from the exhaust of the Teflon chamber while changes to the product mass were recorded by
143 the scale. VOC emission factors (g kg^{-1}) were determined by dividing the integrated VOC signal measured by PTR-
144 ToF over the course of the experiment by the initial mass on the scale and the percentage of mass emitted as VOCs is
145 determined by dividing by the total change in mass on the scale.

146

147 2.3. Mobile and Ground-site Measurements



148 The field measurements used to evaluate ambient measurements of coatings are described in detail by Coggon et al.
149 (2020) and Gkatzelis et al. (2020a). Briefly, measurements were conducted during the New York Investigation of
150 Consumer Emissions (NY-ICE) campaign in winter (March 5 – 28, 2018) and the Long Island Sound Tropospheric
151 Ozone Study (LISTOS) in summer (July 5 – 24, 2018) to characterize the emission profile, strength, and seasonality
152 of VOCs emitted from VCPs.

153 Ground-site measurements were performed at the City College of New York (CCNY) campus. Mobile VOC
154 measurements were conducted throughout NYC and other urban regions (Pittsburgh, Chicago, and Denver) using the
155 NOAA Chemical Sciences Laboratory (CSL) mobile laboratory to characterize the spatial distribution of VCP
156 emissions. The mobile laboratory was driven through the boroughs of New York City, Long Island, and eastern New
157 Jersey, and multiple drives were performed in Chicago (2) and Denver (3). In each case, the mobile laboratory was
158 driven downwind, upwind, and through the city center to evaluate urban VOC enhancements. Drive routes were
159 selected to sample regions of both high and low population density to investigate differences in VCP emissions.

160

161 **2.4. FIVE-VCP Emission Inventory**

162 The Fuel-based Inventory of Vehicle Emissions and Volatile Chemical Products (FIVE-VCP) emission inventory used
163 in this work was described in detail by Coggon et al. (2020). Briefly, VCP emissions were estimated from chemical
164 production data determined from a “bottom up” mass balance of the petrochemical industry. The VOC speciation
165 profiles were updated for the coatings category to include more recent architectural coating surveys by the California
166 Air Resources Board (CARB) (CARB, 2018). The per capita use of VCPs specific to the coating sector was estimated
167 and combined with VOC emission factors (in g VOC per kg product) reported by McDonald et al. (2018a) that is
168 based on a review of indoor air quality literature. The VCP emissions were spatially apportioned using US Census
169 block population data (Bureau USC, 2020a) and the temporal patterns are taken from the National Emissions Inventory
170 (NEI) 2014 (EPA, 2017).

171 Mobile source emissions are estimated utilizing a fuel-based approach based on fuel sale reports for on-road
172 and off-road engines. CO and VOC emission factors (in g VOC per kg fuel) were taken from the compilation by
173 McDonald et al. (2018a) and updated to 2018 by Coggon et al. (2020). The emission factors include tailpipe emissions
174 from running exhaust, enhanced emissions associated with cold-starting engines, and evaporative gasoline VOC
175 sources. The spatial and temporal emission patterns of mobile source engines are taken from the NEI 2014 (EPA,
176 2017).

177

178 **3 Ambient Measurements of PCBTF and Texanol**

179 The NYC ambient measurements of PCBTF and Texanol from the ground site and the mobile laboratory in 2018 are
180 summarized in Fig. 1. In Fig. 1a, the drive tracks overlay a map of the population density in the region and are color
181 coded with summer-time PCBTF and Texanol. The population density is highest in Manhattan with more than 28,000
182 people km⁻². Generally, the highest mixing ratios of PCBTF and Texanol were found in the areas with the highest
183 population density, but were mostly dominated by short, spatially isolated plumes. PCBTF and Texanol were binned
184 along the east-west transects together with the population density as shown in the top panel. The correlations with



185 population density for both compounds ($R^2=0.23$ and 0.57) were lower than what was found for most other VCP
186 tracer compounds ($R^2 > 0.8$, Gkatzelis et al., 2020a). This is consistent with PCBTF and Texanol being from
187 construction activities, rather than correlated with population like other VCP tracers (e.g. D5 siloxane for personal
188 care products). In the lower panel, the time series from the ground site measurements in winter and summer for PCBTF
189 and Texanol are shown together with CO, a combustion tracer, and D5 siloxane, a personal care product tracer
190 (Coggon et al., 2018). At the end of the winter ground-site measurements in late March, a stagnation period, marked
191 in Fig. 1b with the orange box, increased the mixing ratios of all VOCs and CO. The correlations with CO for the
192 winter measurements are also shown in Fig. 1c. Throughout the entire campaign, the correlation of PCBTF and
193 Texanol with CO is low, except for the time period at the end of March (orange) where the urban emissions of near-
194 by sources accumulated at the measurement site. PCBTF and Texanol are also poorly correlated with D5 siloxane,
195 except during the stagnation period ($R^2=0.50$ and $R^2=0.76$). This suggests that PCBTF and Texanol have sources
196 other than combustion and personal care products and the large spikes in PCBTF observed during the drives shows
197 that high emissions are from distinct point sources, and not from dispersed sources like traffic.

198 Even though PCBTF and Texanol have different sources than CO, the correlation with CO during the
199 stagnation event can be used to estimate the PCBTF and Texanol emissions in NYC following the method described
200 by Coggon et al. (2020), which uses the slope from the correlation together with CO emissions from the bottom-up
201 FIVE mobile source inventory (McDonald et al., 2018b). The resulting emissions for PCBTF and Texanol in NYC
202 were approximately 1 and 0.1 mg person⁻¹ day⁻¹, respectively.

203 Figure 2a summarizes the mobile laboratory measurements in Chicago, Pittsburgh, Denver, and the transit in
204 between the cities, where the drive tracks close to the downtown areas in each city are color coded by PCBTF mixing
205 ratio and plotted on top of the population density. Like NYC, PCBTF, and Texanol were generally enhanced in urban
206 regions, but not well correlated with urban population density. PCBTF was significantly enhanced in Chicago in
207 distinct locations, and not well correlated with D5 siloxane (Fig. 2b, $R^2 < 0.1$). The population density dependence of
208 PCBTF and Texanol for winter and summer is shown in Fig. 3a as the ratio of the respective tracer with benzene,
209 which is used as a tracer for mobile source emissions. This ratio controls for meteorology between cities, and also
210 reflects differences in the proportion of VCP and traffic emissions across urban regions. As population density
211 increases, mobile source emissions plateau because of roadway capacity and increased mass transit usage (Gately et
212 al., 2015), while emissions from VCPs scale linearly with the number of people. Consequently, the ratio of a VCP
213 markers (e.g. D5 siloxane) with benzene is higher in more densely populated regions (Gkatzelis et al., 2020a). PCBTF
214 and Texanol do not exhibit a population density dependence ($R^2 < 0.2$), especially compared to D5 siloxane ($R^2=0.82$)
215 (Fig. 1 in Gkatzelis et al. (2020a)), which likely indicates that emissions from coatings are influenced by industrial
216 usage patterns, such as construction activity, rather than consumer product usage patterns, which impact the spatial
217 and temporal variability of D5 siloxane (Coggon et al., 2018; Coggon et al., 2018; Gkatzelis et al., 2020a).

218 The weekly profiles of the PCBTF and Texanol ratios for summer and winter NYC ground site
219 measurements are shown in Fig. 3b. Winter ratios are lower than those in summer, which likely indicates a seasonal
220 change in emissions due to relatively fewer coating projects in the wintertime. The same was observed in the other
221 cities as can be seen in Fig. 3a, where the winter data show a much smaller correlation with the population density



222 compared to summer. In addition to usage trends, it is also likely meteorology accounts for some of changes in
223 emissions between seasons and further complicates interpretation. Texanol ($C_{12}H_{24}O_3$) is detected as a fragment at m/z
224 199 ($C_{12}H_{22}O_2$). It has been suggested that compounds formed via chemical processes are a potential interference at
225 that mass during summer months (Gkatzelis et al., 2020a). A PMF analysis of the ambient dataset used herein is
226 described in detail in Gkatzelis et al. (2020b) and noted that the majority of m/z 199 was attributed to the VCP
227 emissions in summer NYC (>60%), while the remaining fraction was attributed to daytime/morning chemical
228 processes influenced by VOC oxidation. Therefore, photochemistry might contribute to the larger Texanol ratio
229 observed in summer compared to winter and complicates the use of PTR-ToF measured Texanol as a tracer for paints
230 during summer months. Nevertheless, Goliff et al. (2012) observed the highest mean ambient concentrations of
231 Texanol from sorbent-tube collection during summer months in multiple cities, which are unaffected by interferences
232 to other compounds. It might also be expected that coatings emissions are smaller on the weekends compared to
233 weekdays, but this difference is not clearly observed in Fig. 3b. Currently, the FIVE-VCP does not take the seasonality
234 of VCP emissions into account and therefore likely overestimate coatings emissions during winter.

235

236 **4 Headspace and Evaporation Measurements**

237 Gkatzelis et al. (2020a) used the population density dependence of various VOCs to identify specific tracers for VCP
238 emissions. Although PCBTF and Texanol ambient mixing ratios did not show a strong population dependence, they
239 met additional criteria for selection as VCP tracers, i.e., they were regularly measured at significant mixing ratios in
240 ambient air and are uniquely represented in the FIVE-VCP emission inventory as a component of coatings. To
241 demonstrate the prevalence and efficacy of these compounds as markers in the coating VCP category, laboratory
242 measurements were performed to sample VOCs from the headspaces of commonly used architectural coatings and to
243 quantify the fraction of PCBTF and Texanol associated with the measured VOC mass.

244 To understand the composition of the emissions from coating products in greater detail, the headspace of
245 nineteen different coatings were measured by PTR-ToF. To capture the two ends of the spectrum, both a water-borne
246 “zero VOC” low odor paint and a solvent-borne polyurethane stain were tested with the GC-front end pre-separation
247 method described above (GC-PTR-ToF-MS). The GC-PTR-ToF-MS chromatograms of select (a) small oxygenates,
248 (b) hydrocarbons (HC), and (c) aromatics are shown in Fig. 4. For the “zero VOC” paint, the main oxygenate emitted
249 was acetone, with smaller emissions from other solvents including methanol, ethanol, and methylethylketone (MEK).
250 The compounds identified in the “zero VOC” GC hydrocarbon panel are primarily fragments of oxygenated
251 compounds and, generally, oxygenated compounds were the dominant emission from “zero VOC” paint. Emissions
252 from aromatics were negligible. The mass for Texanol and its fragments were observed in the direct PTR-ToF
253 sampling of the headspace of several water-borne products, but pure Texanol injections into the GC-PTR-ToF-MS
254 demonstrated that Texanol does not elute from the GC column either because it is lost to the water trap or has too low
255 of a vapor pressure to elute from the column under the selected temperature program.

256 The GC peaks of the solvent-borne polyurethane in the chromatograms were several orders of magnitude
257 larger than those for the water-borne product. Acetone and MEK were the most abundant small oxygenates, while
258 ethanol and methanol emissions were negligible. Over 30 distinct hydrocarbon peaks were detected with retention



259 times over 300s and with mass 55 ($C_4H_6H^+$) and mass 69 ($C_5H_8H^+$) dominating, which indicates C4- and larger
260 hydrocarbons as the primary constituents. Stoddard solvent is commonly listed as an ingredient in solvent-borne
261 coatings, and mainly consists of < C10 alkanes, cycloalkanes, and aromatics (Censullo et al., 2002), which are clearly
262 evident in the mass spectrum. These hydrocarbons are likely not useful unique tracers for coatings products due to
263 overlapping contributions from gasoline and diesel fuel emission in urban areas (Gentner et al., 2012; Gentner et al.,
264 2013), and therefore a detailed discussion of all the hydrocarbon peaks is beyond the scope of this work. Benzene (m/z
265 79) is one of the aromatics with minor emissions, but most other C7-C12 aromatics including toluene (m/z 93) were
266 more significant. Benzene is often reduced in coating formulations due to its toxicity. The largest aromatic peak is
267 PCBTF, which is completely absent in all water-borne products that were tested.

268 Figure 5a shows PTR-ToF-MS mass spectra during the evaporation experiments of a “zero VOC” low odor
269 paint, primer/sealer paint, a latex paint, and a solvent-borne polyurethane stain. During the evaporation experiments,
270 the products were sampled over longer periods to investigate changes in evaporative emissions. The mass spectra were
271 taken when highly volatile compounds were evaporating early, following initial application of the paint onto the
272 balance, and later when most of the volatile compounds had already evaporated (beyond 3 hours). The mass spectra
273 are given in parts per billion (ppbv) and normalized to the weight loss of the product on the scale in the evaporation
274 chamber. The major peaks in each product are labeled by the most likely compound identification, as determined from
275 fragmentation patterns, headspace analysis, and GC-separation. The sums of all the measured PTR-ToF signals in the
276 “early” mass scan are identified by the labels for all measured VOCs, which includes regulatory-exempt species such
277 as acetone. The pie charts in Fig. 5b show the distribution of VOC mass emitted during each complete evaporation
278 experiment with the largest 10 species labeled.

279 The “zero VOC”, low odor paint and the primer/sealer paint have relatively low emissions, which were
280 dominated by small oxygenated VOCs (methanol, ethanol, formaldehyde, and acetone). The primer/sealer paint also
281 emitted Texanol, which can be expected from the ingredients of many water-borne products. The Texanol signal
282 measured in the laboratory experiments has no contribution from the oxidation products that were identified as
283 potential interferences during ambient summer sampling (Gkatzelis et al., 2020a; Gkatzelis et al., 2020b). Methanol,
284 ethanol, and acetone emissions are expected ingredients, as listed in the FIVE-VCP inventory. Formaldehyde is not
285 an ingredient, but emissions might be expected from the use of preservatives that include formaldehyde-condensate
286 compounds that rely on the release of free formaldehyde from the hydrolysis of a parent structure such as dimethylol
287 glycol and dimethylol urea. Dimethylol glycol and dimethylol urea are routinely used as biocides in water-borne paints
288 and fungicidal products, but have now been widely replaced by other compounds such as isothiazolinones
289 (Salthammer et al., 2010). Ethylene glycol is an abundant ingredient in architectural coatings sales surveys (CARB,
290 2018), and has been observed in an indoor air study during a painting event (Pagonis et al., 2019). The signal at mass
291 45 ($C_2H_4O \cdot H^+$) is typically attributed in PTR-MS studies to acetaldehyde (de Gouw and Warneke, 2007), but ethylene
292 glycol fragments mostly to m/z 45. Acetaldehyde was present in the GC experiments and although ethylene glycol
293 was not observed, as it is likely lost in the water trap, its dominance in architectural coatings and paints suggests it
294 may be a dominant species at that mass.



295 The total VOC signal was significantly larger by an order of magnitude for water-borne latex paint than for
296 the two other water-borne paint products, with ethanol being the biggest emission. In addition to the small oxygenated
297 VOCs, larger compounds such as dipropylene glycol monobutylether and other ketones and acetates were emitted.
298 Several species listed as ingredients in CARB coatings surveys were tentatively identified in the paint emissions as
299 ethylene glycol, methyl-n-amyl ketone, 1-methyl-2-pyrrolidinone, and methyl-, vinyl-, ethyl-, and butyl acetate. For
300 butyl acetate, the major peak in the GC chromatogram at mass 117 correlated strongly with peaks at m/z 61 and 43,
301 which are known fragments of the parent ion (Buhr et al., 2002).

302 As was expected from the GC analysis, the VOC emissions of the solvent-borne polyurethane were markedly
303 different and ~5 times larger than the water-borne paint. Hydrocarbons and aromatics are clearly evident in the mass
304 spectrum. Small masses ($C < 5$) are known to be affected by fragmentation, which adds to quantification uncertainty,
305 and most hydrocarbon masses had multiple peaks in the GC chromatograms. As was noted in the headspace GC
306 experiments, the solvent-borne polyurethane also emitted PCBTF.

307 The weight loss recorded on the scale during the evaporation experiments equals the mass emitted as VOCs,
308 water (which was not measured), and other compounds undetectable by PTR-ToF. Each measured VOC (mg m^{-3}) was
309 converted to an emission rate (mg s^{-1}) by multiplying with the gas flow rate and integrated across the length of the
310 experiment to determine the total mass emitted by each individual species. Figure 6 shows the time series of mass
311 emitted as the sum of all measured VOCs overlaid with the weight change measured on the Teflon covered scale for
312 each evaporation experiment.

313 For the water-borne products in Fig. 6a-c, the mass emitted as VOCs is a very small fraction of the mass lost
314 from the coatings product (<1 to 7%) and the main weight loss is attributed to water. Fig. 6b shows the time series for
315 the primer/sealer paint, which was the product with the largest difference in VOC emission rate and mass lost. This
316 mass loss rate gradually leveled off, while the total VOC emission continued to increase at a steady rate. This was
317 largely driven by only a few compounds (e.g. ethylene glycol), and therefore the estimated mass loss and emission
318 factors reported herein represent lower-end estimates. Latex paint showed a similar behavior with VOCs steadily
319 rising even at the conclusion of the experiment. These results are not unexpected, as emissions of Texanol from paints
320 have been observed for periods as long as 15 months (Lin and Corsi, 2007) and these experiments were stopped after
321 19 hours. The VOC mass emitted, as detected by PTR-ToF, is related to the VOC content of the product, where the
322 latex paint clearly has the largest VOC emission and the “zero VOC” paint the lowest.

323 For the solvent-borne polyurethane coating in Fig. 6d, the mass emitted as VOCs exhibited a temporal profile
324 that more closely mirrored the mass lost recorded by the scale. The similarity in the emission profile and weight loss
325 indicate that the majority of the weight loss from the solvent-borne stain is due to VOC emissions with only a small
326 fraction of weight loss from other undetected compounds or underestimation due to poor sensitivity to hydrocarbons.
327 The mass remaining on the scale indicated that about 40% of the weight remained as solids or unevaporated VOCs,
328 which is within 5% of what is expected from the manufacturer reported VOC content of 550 g L^{-1} . Figures 6b and 6d
329 represent two extremes and it is likely each product will have different evaporative properties depending on the overall
330 composition and atmospheric conditions. Figure 6 also shows that for the (a) “zero VOC” paint and (d) polyurethane
331 stain, the VOCs emitted in the first hour account for over 50% of the total mass emitted as measured VOCs over the



332 course of this experiment. Latex paint (c) takes an additional hour and the primer/sealer (b) takes nearly 6 hours for
333 the majority of the measured VOCs to evaporate. The experiment did not complete to dryness, thus the total mass
334 measured is likely an underestimate, and potentially under-account semi- and intermediate-volatility VOCs that have
335 a lower volatility. Continued emissions from dry-paint have been observed following complete water evaporation
336 (Clausen, et al., 1991; Hodgson et al., 2000), though emissions from the dry-film were not investigated here.

337 Figure 7a shows the time series of the emission rates of the sum of all measured VOCs for each product (mg
338 h⁻¹). The solvent-borne polyurethane had a maximum VOC emission rate (6.7 mg h⁻¹) that was more than a factor of
339 two greater than the highest-emitting water-borne coating. For each product, the highest total VOC emission rate
340 peaked within the first 6 minutes. The elapsed time to reach the maximum emission rate varied to within a few minutes,
341 and this likely reflects the different volatilities of the ingredients. For the coatings tested here, the majority of the
342 measured VOC mass is emitted within the first few hours, and therefore the most significant atmospheric implications
343 for ozone formation likely occur during and shortly following application.

344 Figure 7b shows the relative contribution of select VOCs to the total VOC mass as a function of time during
345 the evaporation of the primer/sealer paint. Emissions of methanol and 1-butanol fragments dominated at the start of
346 the experiment, followed by other species including ethylene glycol and Texanol, which all peaked in a sequence that
347 paralleled reported saturation vapor concentrations (NIST Chemistry WebBook). The volatilities of candidate species
348 at mass 45 suggest ethylene glycol ($C_0 \sim 10^5 \mu\text{g m}^{-3}$) is the dominant compound, since the emissions of acetaldehyde
349 ($C_0 \sim 10^9 \mu\text{g m}^{-3}$) would have peaked before methanol ($C_0 \sim 10^8 \mu\text{g m}^{-3}$). The emissions of acetone and formaldehyde
350 are more complicated. Although the reported saturation vapor pressures are higher than methanol the maximum
351 emission rate peaked later and changed more gradually, resulting in more prolonged emissions. It is clear that the
352 contribution of specific compounds to the total mass emitted can vary significantly over time and likely depends on
353 volatility (C_0), the initial composition of the product, and other factors such as drying time, temperature, humidity,
354 and substrate interaction/properties. Texanol has a lower saturation vapor concentration ($10^5 \mu\text{g m}^{-3}$), and the
355 maximum emission rate occurred ~11 minutes into the experiment, but the amount of mass emitted as Texanol during
356 the first hour only accounted for 34% of the total Texanol emitted during the entire experiment (~19 h). It took over
357 6 hours to account for 75% of the total emitted Texanol, demonstrating that certain species can emit considerably
358 across several hours to days. The majority of the Texanol emission does occur within the first several hours, and the
359 fast evaporation supports its use as a tracer. Lin and Corsi (2007) showed emissions of Texanol decreased by 90%
360 within the first 100 h following paint application, and mass closure assessments showed that airborne emissions of
361 Texanol were greater than recovery from material components for thin-film flat paints. The VOC speciation in each
362 evaporation experiment is shown in Fig. 5b.

363 The PTR-ToF also detects several inorganic species such as ammonia, though the signal at m/z 18 suffers
364 from high background signal and has only been quantified for large emission sources such as biomass burning (Karl
365 et al., 2007; Müller et al., 2014; Koss et al., 2018). There was a clear enhancement of ammonia in all water-borne
366 coatings that was absent in the solvent-borne coatings, and it is likely mass emitted as ammonia can be important in
367 water-borne products as it is commonly used as a pH stabilizer. The ammonia PTR-ToF sensitivity derived from a
368 comparison with an FTIR during biomass burning sampling (Koss et al., 2018) was used to estimate the mass emitted



369 as ammonia for the latex paint. The total mass emitted as ammonia (2.1 mg) rivaled the VOC mass (2.3 mg), and
370 shows ammonia emissions can be significant from certain water-borne products. There was no direct calibration of
371 ammonia during these experiments and therefore the discussion focuses on VOCs only.

372 Table 1 summarizes the results of the evaporation experiments. As expected, the solvent-borne polyurethane
373 VOC emissions accounted for the greatest amount of total mass detected (83%), which is likely a lower limit estimate
374 since the PTR-ToF is less sensitive to hydrocarbons. The trend in the VOC emissions tracks the VOC content reported
375 on the product labels (g L^{-1}). The “zero VOC” paint data sheet reported $< 5 \text{ g L}^{-1}$ VOCs and emitted very few VOCs
376 with an emission factor (in $\text{g VOC emitted per initial weight of the product}$) of $0.7 \text{ g VOC kg}^{-1}$ paint, followed by the
377 primer/sealer (2.8 g kg^{-1}), latex paint (43.1 g kg^{-1}), and finally polyurethane (495 g kg^{-1}) with a reported VOC content
378 of $< 550 \text{ g L}^{-1}$. The VOC emission rates for each product, averaged during the 19-hour experiments, also mirror the
379 VOC content. We note that the emission factors are underestimated since the experiments did not complete to dryness.

380

381 **5 CARB Architectural Coatings Survey Data**

382 Every four to five years, CARB conducts comprehensive surveys of architectural coatings sold in California to gather
383 information about the ingredients and sales with the goal of updating emission inventories. The response to the surveys
384 is mandatory and CARB ensures the validity of the data following extensive quality assurance and quality control
385 measures and the results accurately represent the sales volume in California. The data are publicly available (CARB,
386 2018). Speciation is based on reported product formulations and emissions data reflect applicable fate and transport
387 adjustments.

388 Figure 8a shows the trend in sales and emission estimates for the last five surveys from 1990 to 2014. The
389 sales volume increased significantly from 1990 to 2004, but was lower in 2014 as the industry was still recovering
390 from the economic recession in 2007-2009 that led to a sharp decline in construction spending (Bureau USC, 2020b).
391 During this time, coating emissions continuously decreased from 126 tons/day to < 27 tons/day in California. Most of
392 the sale volume was associated with water-borne coatings, and the fraction increased to $\sim 75\%$ of the total in 1990 to
393 $\sim 93\%$ in 2013. The emissions, on the other hand, were dominated by solvent-borne coatings with $> 72\%$ of the total
394 in 1990 and half solvent-borne and water-borne each in 2014. This shows that the VOC content, and therefore the
395 emissions, of coatings in total have significantly decreased since the 1990s. Furthermore, the higher-emitting solvent
396 borne coatings are increasingly being replaced by water-borne products, which together resulted in this significant
397 emission reduction. The CARB survey also separates the sale and emissions into the different product categories (not
398 shown). Common water-borne paints, such as flat or low-gloss coatings and the accompanying primer, make up the
399 bulk of the total sales, but only about half of the emissions. In contrast, solvent-borne products such as stains,
400 varnishes, or rust preventative coatings are sold in lower volumes, but contribute the other half of the coating
401 emissions.

402 The South Coast Air Quality Management District (SCAQMD) also reports data from coatings sales and
403 emissions from 2008 to 2017 (reproduced in Fig. 8b). These data are part of the CARB survey and represent half of
404 the California-wide emissions. The sales in SCAQMD have been relatively steady ranging from 35–42 million gallons
405 with only slight increases since 2009, while the emissions have decreased significantly from 2008 to 2014 and were



406 constant around 11 tons/day from 2014 until 2017. This data set extends the CARB surveys and might indicate that
407 the overall emissions have not continued the steep decrease after 2014, so that 2014 CARB data might still be
408 representative of the 2018 ambient measurements presented above.

409 The VOC ingredients of coatings reported in the CARB surveys have also changed significantly from 2005
410 to 2014. The left panels of Fig. 9a show the top 35 non-exempt VOC ingredients out of over 300 in the survey, together
411 with the exempt ingredients for 2005 and 2014 in the right panel. As was already clear from Fig. 8, the total amount
412 of VOC ingredients significantly decreased from 73 million pounds in 2005 to 23.6 million pounds in 2014, but also
413 the composition has changed. For example, in 2005 xylene was still a major ingredient of coatings but does not show
414 up in the top 35 ingredients in 2014. Even though the total amount of exempt ingredients stayed almost constant, the
415 relative amount has increased to almost 20% in 2014 from about 7% in 2005. The hydrocarbons from solvents are
416 generally the largest emissions, but small oxygenated VOCs, such as ethylene glycol, propylene glycol, acetone, and
417 ethanol, are also strongly emitted by paints and coatings and were detected as significant emitters in the laboratory
418 experiments. The ingredients measured as emissions in the ambient or laboratory experiments by the PTR-ToF are
419 indicated as solid bars in Fig. 9a for the 2014 data.

420 Most of the VOC ingredients shown in Fig. 9a are not unique to coatings products, but Texanol and PCBTF
421 are two compounds that are used only in coatings products as can be seen in Fig. 9b, where the fractions of VCP
422 emissions in the coatings category of various VOCs are shown. The compounds are sorted by their contribution to the
423 coatings category according to the FIVE-VCP inventory calculated using the method of McDonald et al. (2018a). The
424 only other compound besides Texanol and PCBTF that is predominantly attributed to coatings in the FIVE-VCP is
425 methylene chloride, but the amount used is too small to be a useful atmospheric tracer.

426 All the VOC ingredients collected by the CARB survey might not necessarily be emitted by the products; for
427 example Texanol airborne recoveries were between 25-90% depending on the paint and the substrate (Lin and Corsi,
428 2007) and in addition reactions and polymerization will occur in the production of the chemical products. The
429 ingredients that have been detected in either the evaporation experiments or the ambient measurements with the PTR-
430 ToF are indicated as solid bars for the 2014 data in Fig. 9a. Texanol emitted during evaporation of the primer/sealer
431 paint accounted for 13% of the measured VOC emissions. The ingredients reported in the CARB 2014 survey indicate
432 Texanol was 10% of the total VOC ingredient sales including exempt VOCs. The agreement between the laboratory
433 measurement of Texanol and the ingredients summary is reasonable considering the range in airborne recoveries.
434 PCBTF in the solvent-borne polyurethane only accounted for 0.2% of the total VOC mass as compared to the reported
435 ingredient sales contribution of 9%. These results demonstrate the challenges in generating a representative emissions
436 inventory from product sales as each product has a unique composition and ingredient sales do not necessarily equal
437 emissions. It is also possible that uses of PCBTF could differ between formulations available to consumers and those
438 used for professional industrial applications. Only a small selection of commercially available coatings were tested
439 here.

440 More details of the use of PCBTF and Texanol are shown in Fig. 10, where panel (b) shows that the use of
441 Texanol has strongly declined, while the use of PCBTF has increased such that they had comparable ingredients sales
442 in 2014. Both were around 10% of the total sale each. The pie charts in Fig. 10a show that PCBTF is mainly used as



443 a solvent in solvent-borne products, such as sealers, stains and polyurethane finishers. Texanol is used in water-borne
444 products as a coalescent for latex and other paints (Lin and Corsi, 2007). In summary, the CARB survey results in
445 Fig. 8, 9, and 10 indicate that PCBTF might be a good atmospheric tracer for solvent-borne coatings and Texanol for
446 water-borne coatings, even though the use of Texanol is rapidly declining.

447

448 **6 Conclusion**

449 Mobile field measurements in urban areas show that compounds largely associated with architectural coatings, such
450 as PCBTF and Texanol, were observed from point source locations near and around construction activity. Unlike other
451 VCP emissions previously described by Gkatzelis et al. (2020a), these molecules do not correlate strongly with
452 population density, which suggests that their emissions are not driven by wide-spread, individual usage. In contrast,
453 the spatial and temporal patterns suggest that coating emissions are from discrete industrial applications, such as
454 architectural and construction projects.

455 Headspace analysis measured with a PTR-ToF and GC front end confirmed the identity of many VOCs
456 cataloged as ingredients in inventories compiled by CARB from architectural coating surveys. The “zero VOC” paint
457 analyzed had low VOC emissions dominated by small oxygenates including methanol, ethanol, and acetone, with
458 negligible emissions from smaller hydrocarbons and aromatics. The solvent-borne polyurethane stain emissions were
459 compositionally different with the distribution shifted largely towards hydrocarbons and aromatics with a clear
460 enhancement of PCBTF. The emission rates (mg s^{-1}) were calculated for each VOC and the total mass emitted as
461 VOCs was calculated for the length of a controlled evaporation experiment and compared to total product mass
462 emitted. The VOCs accounted for a range of 0.2-83% of the total mass emitted with the relative contribution mirroring
463 the VOC content (g L^{-1}) reported by the manufacturer. Inorganic species such as ammonia were detected in water-
464 borne coatings and likely contribute to some evaporative mass loss, though their contribution was not quantified in
465 this study. The total VOC emission rates were highest within the first 6 minutes of application and for three of the
466 four products, over 50% of the total VOC mass was emitted within the first two hours. These results highlight the
467 importance of the initial evaporative emissions of coatings following application events, as they likely have important
468 impacts on ozone.

469 Finally, reported sales and usage trends were compared to ingredients compiled in architectural coatings
470 surveys, and show Texanol and PCBTF are unique to coatings. Although Texanol use has strongly declined and
471 PCBTF has increased, they had comparable ingredients sales in 2014 at around 10% of the total. The prevalence and
472 distinct usage of these VOCs support the assignment of PCBTF and Texanol as tracers for solvent- and water-borne
473 coatings, respectively.

474

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477 **Data availability**

478 The data from the laboratory tests are available on request. Ambient data from the NYICE 2018 are available here:
479 <https://esrl.noaa.gov/csl/groups/csl7/measurements/mobilelab/MobileLabNYICE/DataDownload/index.php?page=/csl/groups/csl7/measurements/mobilelab/MobileLabNYICE/DataDownload/>

481



482 ***Author Contributions***

483 MMC, CW, JBG, GIG, JO and carried out the laboratory experiments. JO designed and built the GC inlet system.
484 Ambient measurements were collected by MMC, GIG, JBG, KA, and JP. FIVE-VCP inventory work was completed
485 by BCM and MT. CES and CW conducted data analysis and wrote the manuscript. All authors contributed to the
486 discussion and interpretation of the results.

487

488 ***Competing Interests***

489 The authors declare that they have no conflict of interest.

490

491 ***Disclaimer***

492 Mention of commercial products is for identification purposes only and does not imply endorsements.

493

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496

497



498 **7 References**

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Product	Mass emitted as measured VOCs	VOC Emission Factor	Labeled VOC content	Average VOC emission rate	Maximum VOC emission rate
	%	g kg⁻¹	g L⁻¹	mg day⁻¹	mg hr⁻¹
Polyurethane stain	83	495	550	20.6	6.69
Latex paint	6.63	43.1	250	2.33	3.16
Primer/sealer paint	0.66	2.84	100	0.22	0.03
"Zero VOC" paint	0.17	0.71	< 5	0.04	0.14

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Table 1: Summary of the evaporation experiments for four coating types including percentage of mass lost as measured VOCs (%), VOC emission factors (g kg⁻¹ paint), reported product label VOC content (g L⁻¹), and the average and maximum total VOC emission rates. Note: emission factors are lower-end estimates calculated based on the length of these experiments

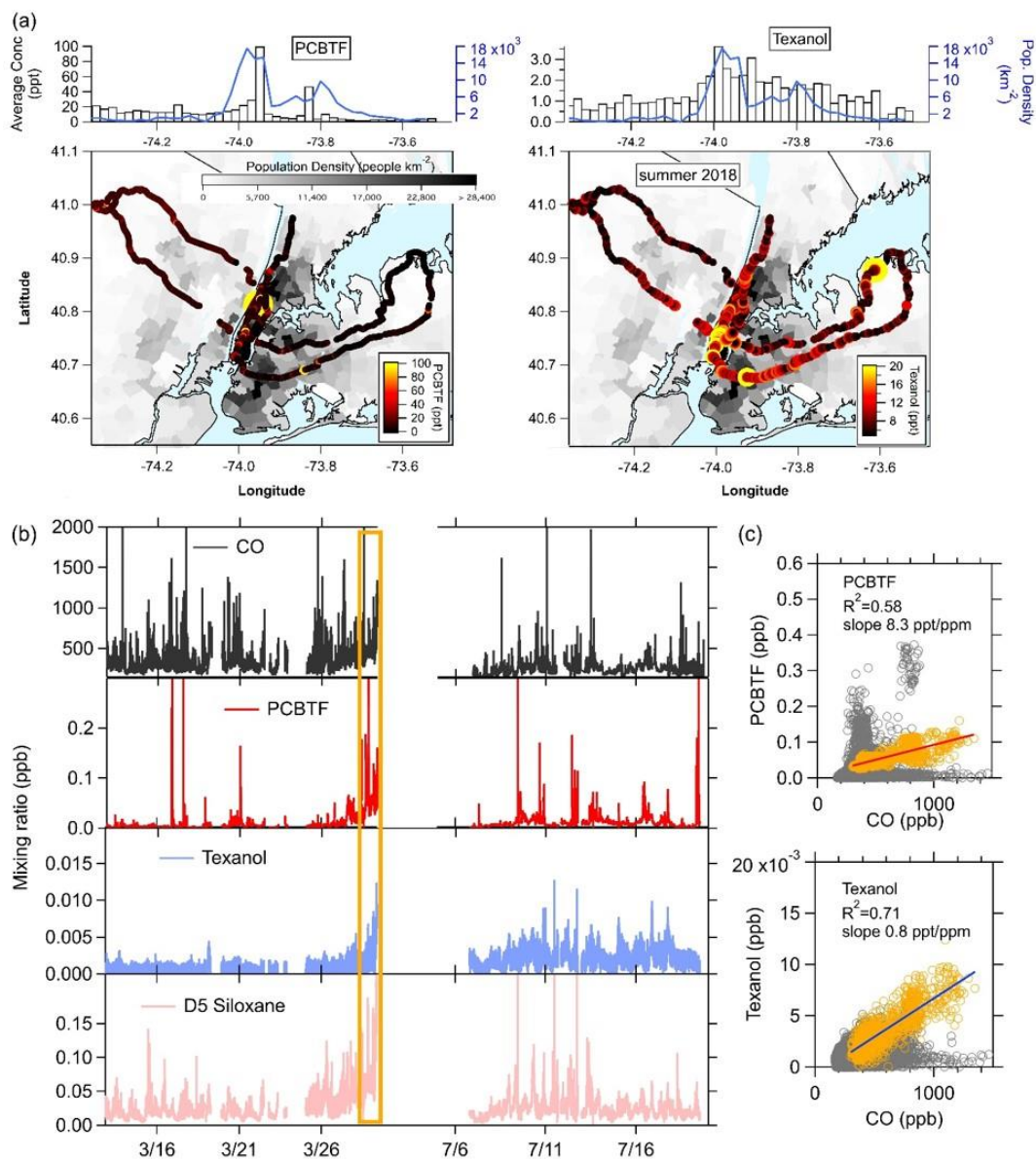


Figure 1: Summary of the PCBTF and Texanol measurements in New York City: (Map) Color-coded NOAA Mobile Laboratory drive track on a map of the population density. (a) Binned population density and mixing ratios. (b) Time series of CO, PCBTF, Texanol, and D5 siloxane for winter and summer months. The stagnation period during winter measurements is highlighted in orange. (c) The correlation plots of PCBTF and Texanol with CO for winter measurements. Slopes are calculated for the stagnation period at the end of the winter measurements (orange).

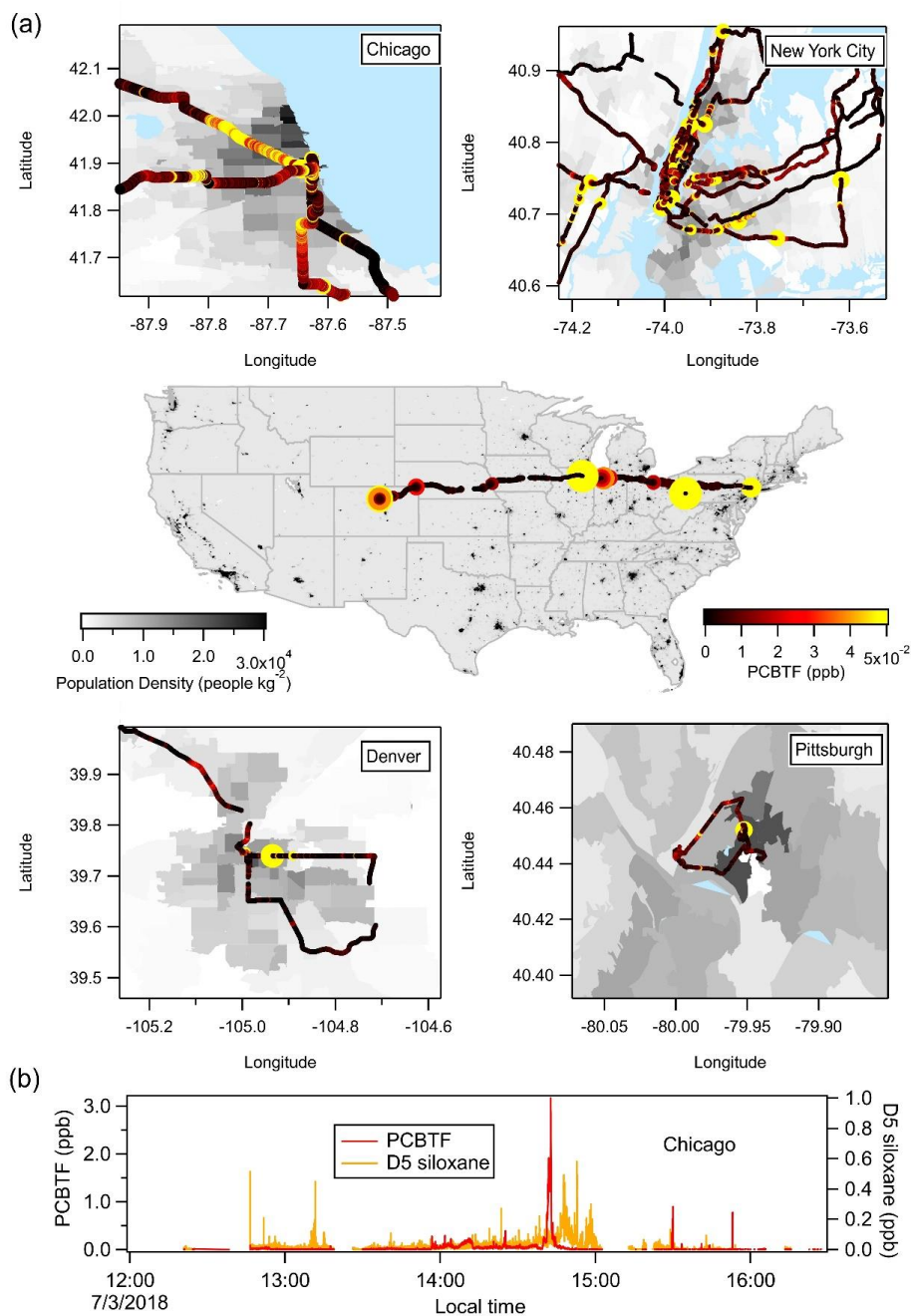


Figure 2: (a) Summary of the PCBTF and Texanol measurements from Chicago, New York City, Denver, and Pittsburgh. (b) Time series of PCBTF and D5 siloxane during Chicago drives.

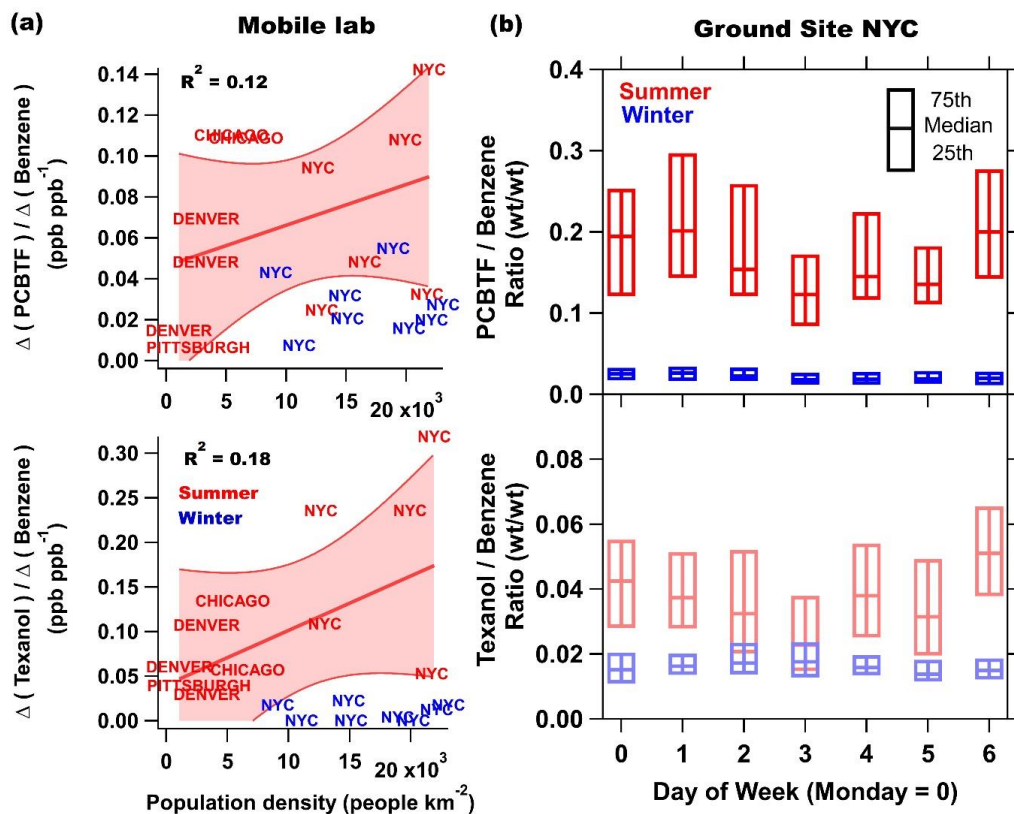
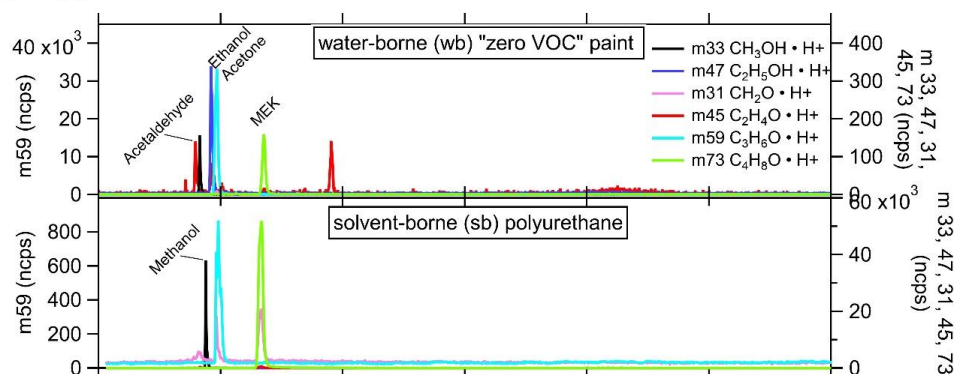


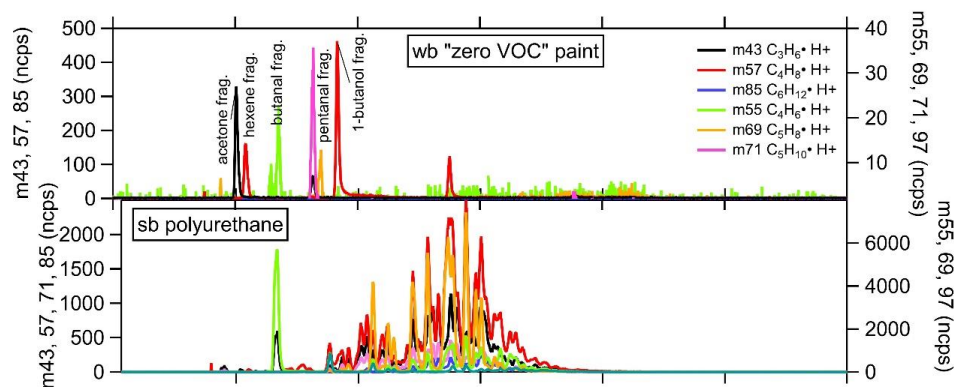
Figure 3: (a) The enhancement of PCBTF and Texanol relative to the enhancement of benzene versus the population density in summer (red) and winter (blue) in various cities. Denver and Chicago are represented by multiple drives. NYC is an average of all drives throughout the city, but separated by regions with high (19,000 - 23,000 people km⁻²), medium (14,000-19,000 people km⁻²), and low (9,000-14,000 people km⁻²) population densities. (b) The summer and winter weekly profile of the PCBTF and Texanol versus benzene ratio.



(a) Oxygenates



(b) Hydrocarbons



(c) Aromatics

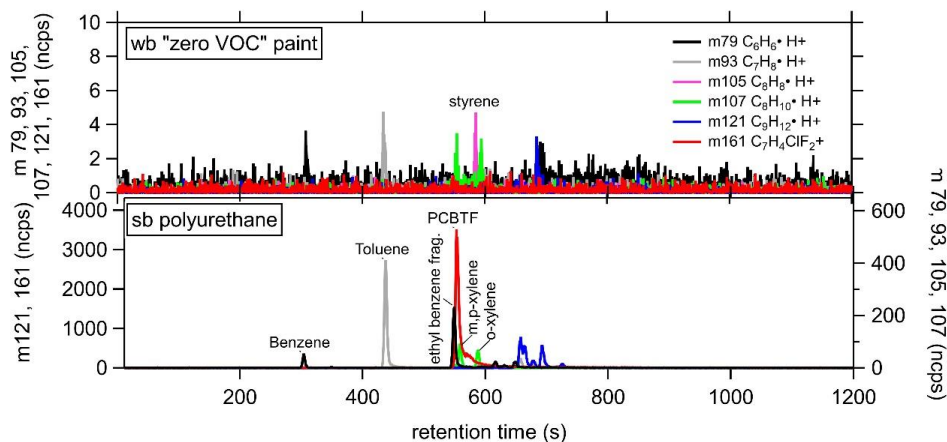


Figure 4: GC-PTR-ToF chromatogram from the headspace of a water-borne (wb), "zero VOC" low odor paint with ink and a solvent-borne (sb) polyurethane stain for (a) small oxygenates, (b) hydrocarbons, and (c) aromatics.

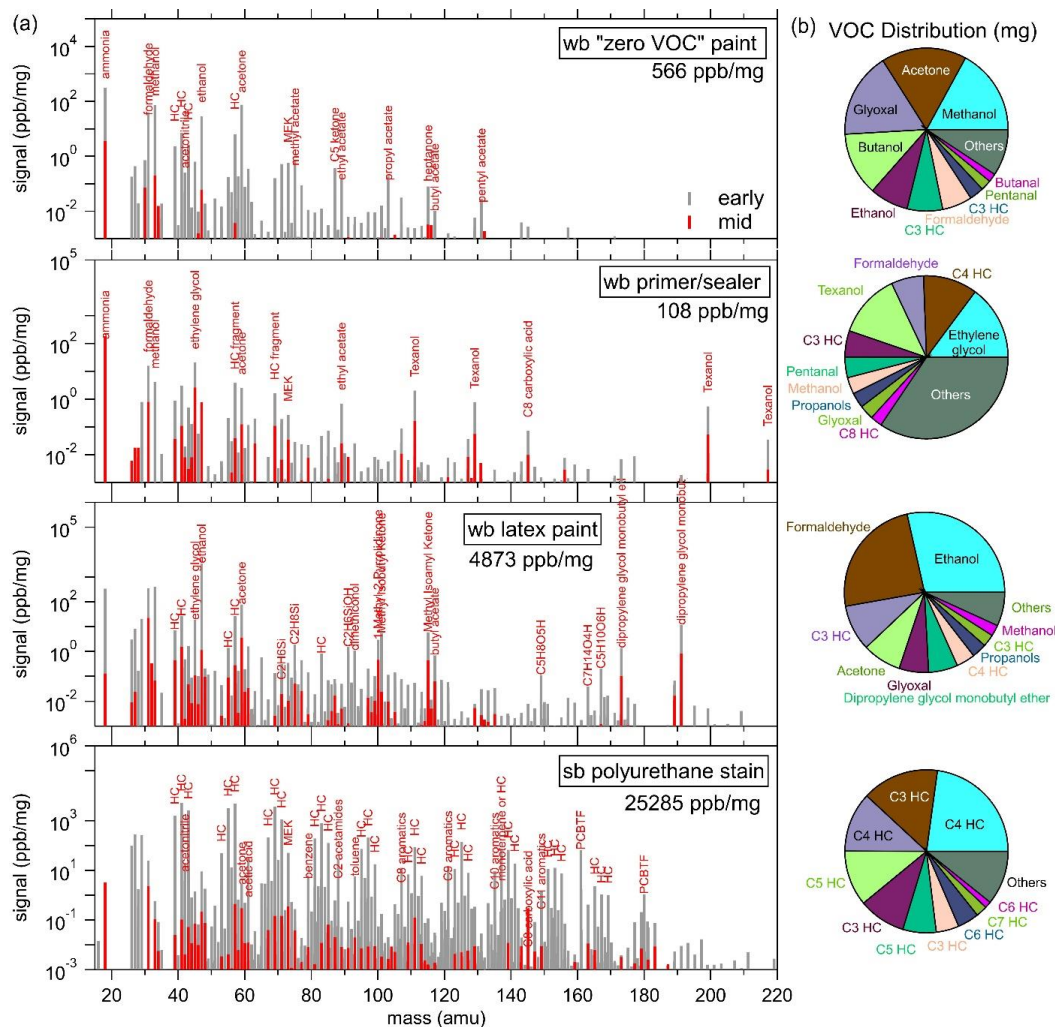


Figure 5: (a) PTR-ToF-MS mass spectra of a water-borne (wb) low VOC paint, a wb primer/sealer paint, a wb latex paint, and a solvent-borne (sb) polyurethane stain, where the major peaks are labeled by their most likely identification. The values in ppbv are normalized to the weight loss of the product on the scale during the evaporation experiment. In each panel a mass spectra in the early part (grey) of the experiment and one in the middle part (red) are shown. The total VOC signal per mg of product is indicated in the legend. (b) Pie charts of the total mass emitted by individual VOCs during evaporation experiments.

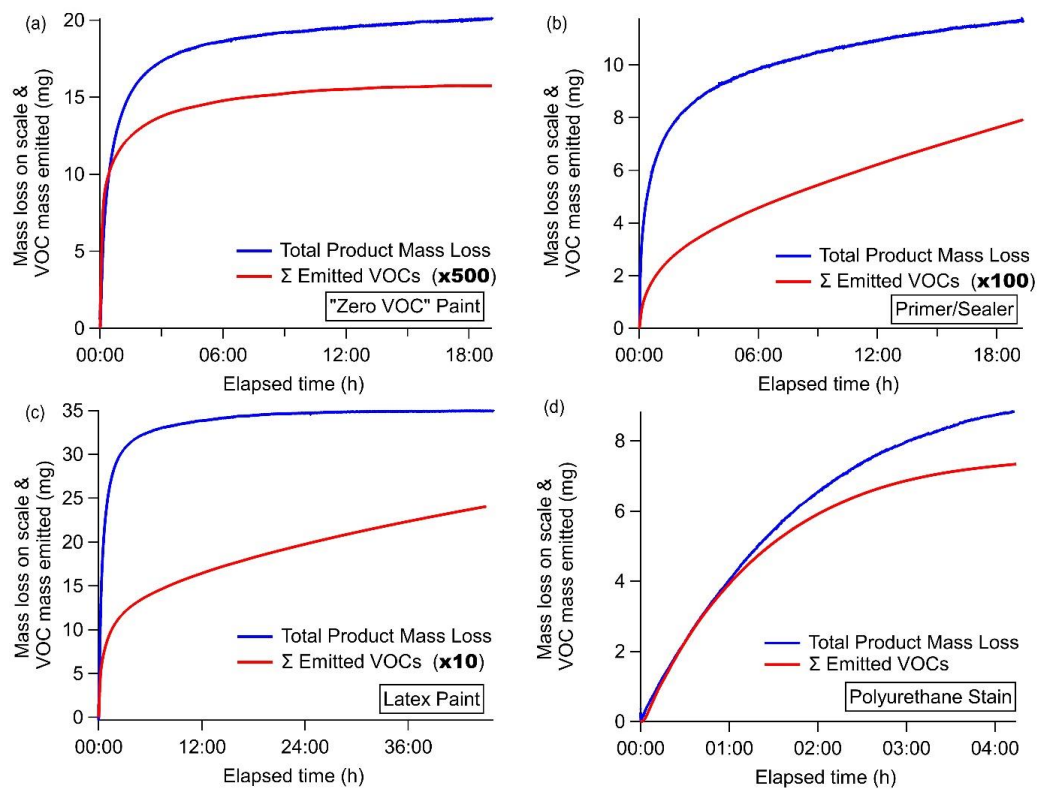


Figure 6: Total product mass loss measured on the scale (blue) overlaid with the total mass emitted as VOCs (red) measured by the PTR-ToF-MS as a function of elapsed time. The emitted VOC scalar is indicated in the legends.

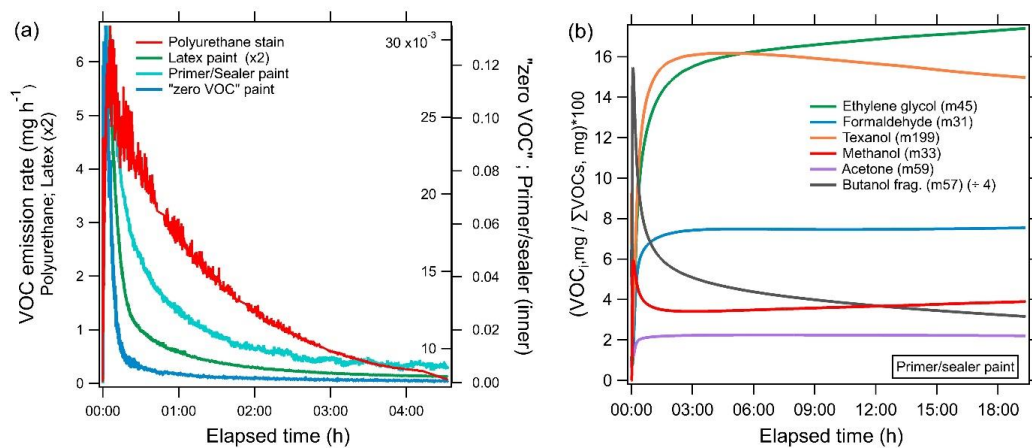


Figure 7: (a) Emission rates (mg h^{-1}) of all measured VOCs summed during evaporation experiments of different coating types: polyurethane stain (red), latex paint (green), primer/sealer paint (cyan), "zero VOC" paint (blue). (b) Time series showing the percent of mass emitted as an individual VOC (VOC_i) to the total measured VOC mass for the evaporation of the sealer/primer paint. The most likely identity and detected mass of individual VOCs are indicated in the legend.

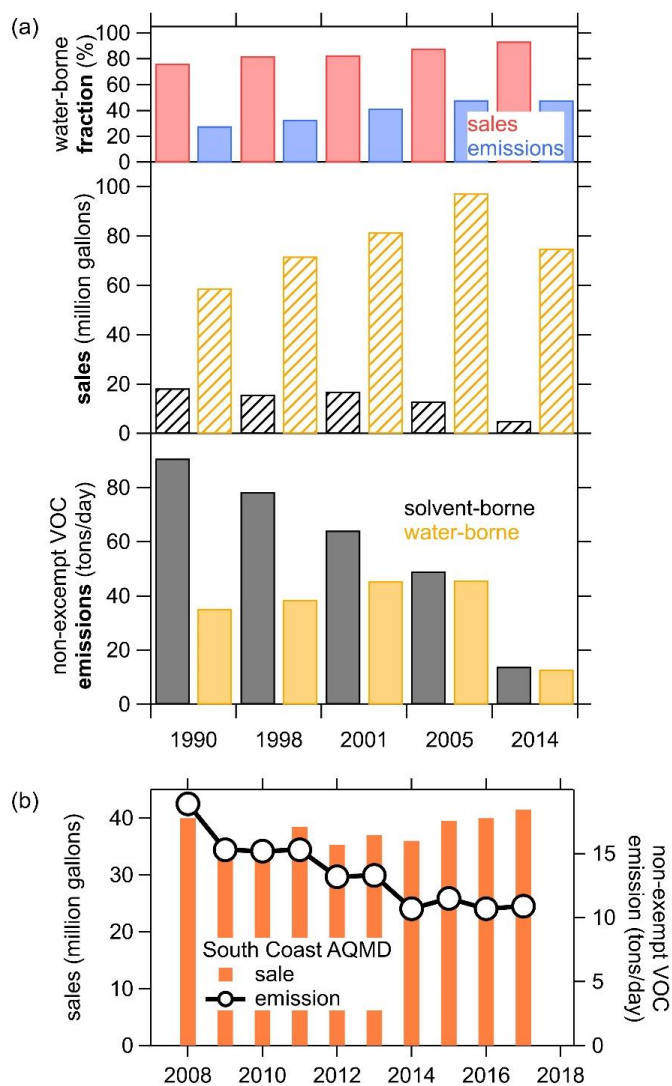


Figure 8: (a) Trends in paints and coatings sales and VOC emissions from the CARB coating surveys since 1990. (b) South Coast AQMD trend of coatings reproduced from: <http://www.aqmd.gov/home/rules-compliance/compliance/vocs/architectural-coatings>

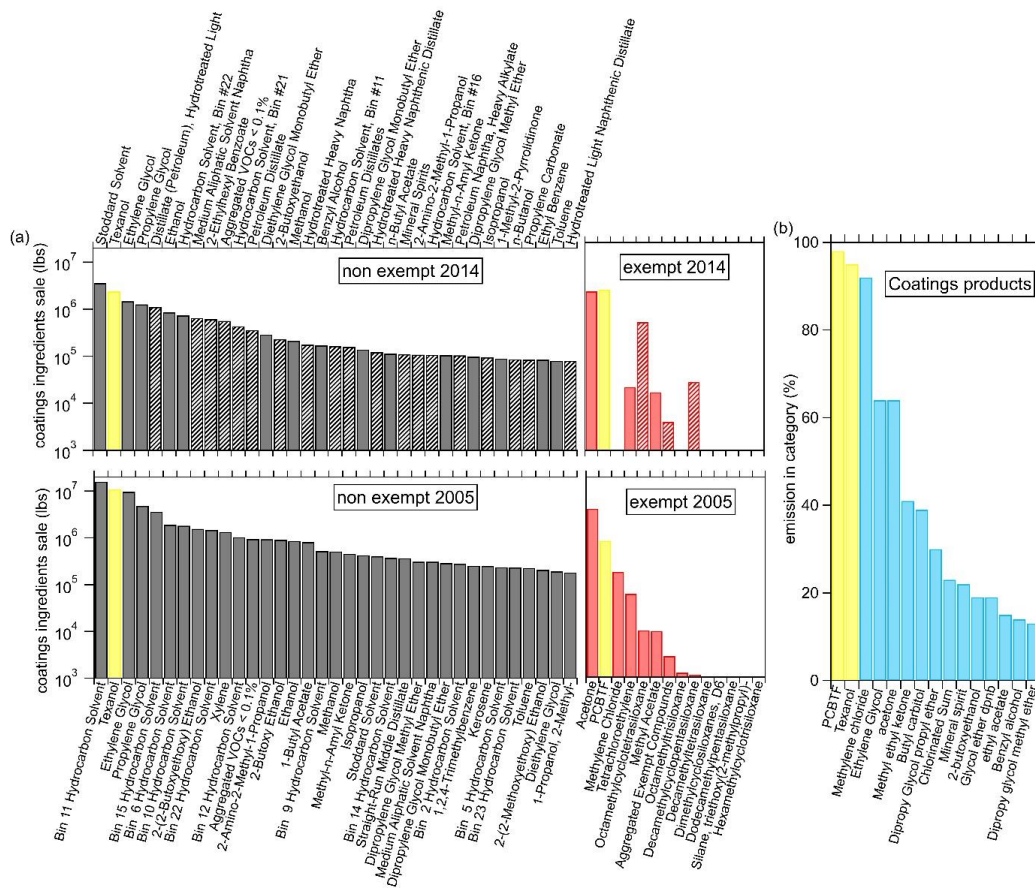


Figure 9: (a) The sale of top 35 non-exempt and the exempt VOC ingredients for coatings in 2005 and 2014 in California together with the (b) fraction of emissions in the coatings category of the 15 highest VOCs as determined by the FIVE-VCP inventory calculated using the method of McDonald et al. (2018a). The solid bars in the 2014 data indicate compounds that were detected in ambient or product testing.

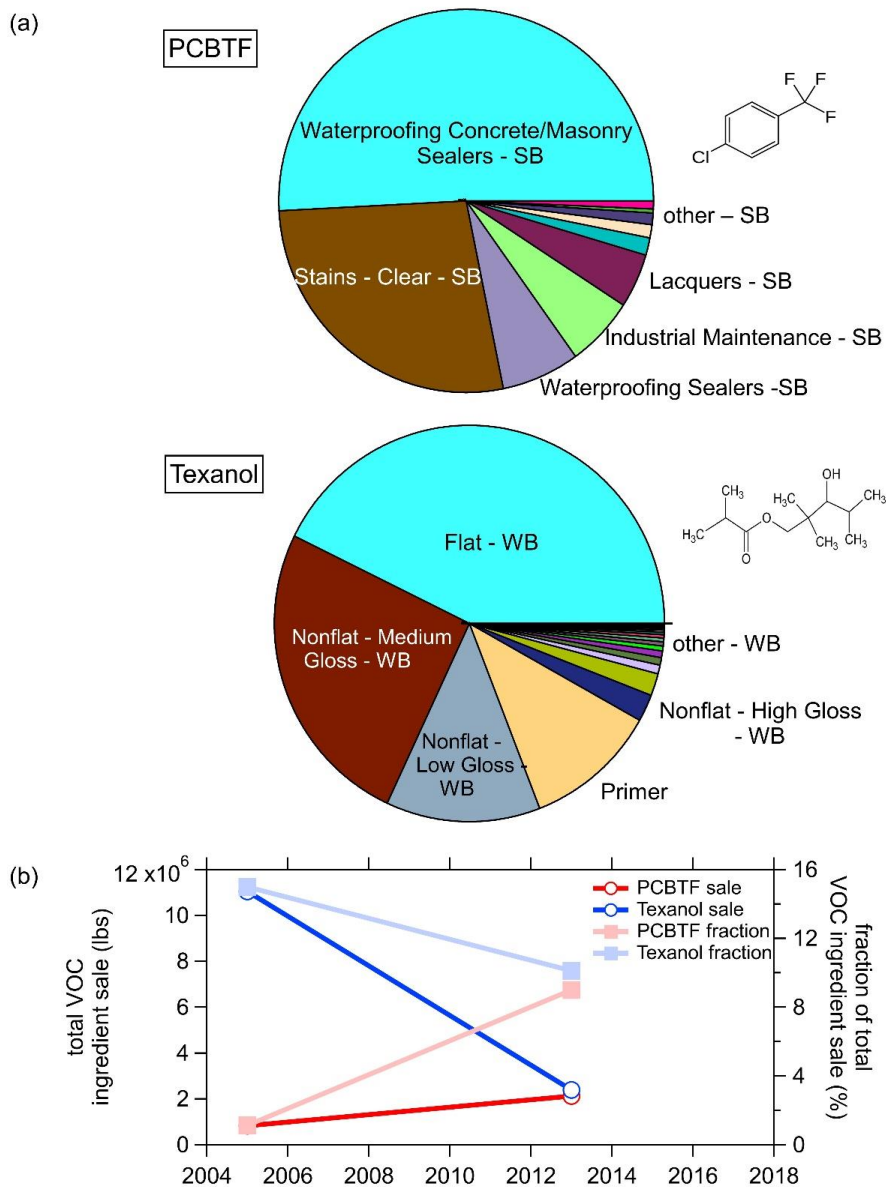


Figure 10: (a) PCBTF and Texanol use in solvent-borne (SB) and water-borne (WB) product categories in California and their (b) trends in sales and emissions.