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

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

1 Introduction

After decades of declining mixing ratios of volatile organic compounds (VOCs) in urban areas from combustion-related processes (Warneke et al., 2012), emissions from volatile chemical products (VCPs = coatings, adhesives, inks, personal care products, pesticides, and cleaning agents) have emerged as a major source of VOCs of petrochemical organics in the urban atmosphere (McDonald et al., 2018a). Measurement and modeling efforts have already shown that VCP emissions and their contribution to urban ozone formation are comparable to those for fossil

38   fuel VOCs in Los Angeles and other cities in the United States (McDonald et al., 2018a; Coggon et al., ~~2020~~2021).

39   Reductions in tailpipe emissions of VOCs from gasoline vehicles are slowing, and diminishing returns from emission

40   control technologies have been reported for on-road vehicles (Bishop and Haugen, 2018). With slowing trends in

41   ozone precursors and shifts in ozone production regimes, decreases in ozone design values may have slowed as well

42   (Parrish et al., 2017).

43   A fuel-based inventory by McDonald et al. (2018a) showed that about 18% of the petrochemical VOC

44   emissions in Los Angeles in 2010 were from personal care products. Coggon et al. (2018) found that D5 siloxane,

45   which is a unique tracer for personal care product emissions, is emitted in urban areas in similar amounts as benzene

46   from vehicles, indicating a significant emission source of personal care products. The next largest emission source

47   was from coatings accounting for approximately 13% of the VOC inventory in Los Angeles. Coatings in emission

48   inventories are defined as paints, varnishes, primers, stains, sealers, lacquers, and other solvents associated with

49   coatings (e.g., thinners, cleaners, additives). This includes both industrial and architectural ~~uses~~coatings, which

50   comprise half-and-half of the coating fraction. Architectural coatings are defined as products applied to stationary

51   structures and their accessories, whereas coatings applied in shop applications or to non-stationary structures are

52   categorized as industrial coatings. Both coating types can be utilized in industrial applications (e.g., construction or

53   manufacturing activities). The impact of VOC emissions from coatings has been investigated in the indoor

54   environment (Corsi and Lin, 2009; Weschler and Nazaroff, 2012; Schieweck and Bock, 2015; Kozicki et al., 2018),

55   but few measurements have been reported in the outdoor environment. Urban air is likely impacted from coating

56   emissions from indoor/outdoor exchange as well as from architectural and industrial coating usage outdoors. To

57   quantify VCP coating emissions in urban air, it is important to identify VOC tracers that are uniquely linked to water-

58   and solvent-borne usage, analogous to the emissions of D5 siloxane from personal care products. Although there is a

59   lack of detailed analysis of coatings emissions in the ambient atmosphere, emissions suspected from coatings have

60   been measured in ambient air. Goliff et al. (2012) measured 2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (TPM,

61   also known as Texanol®), a common solvent in water-borne coatings, in Southern California at mixing ratios of up to

62   20 ppt with the largest values in summer, when coating activities are typically the highest.

63   The composition and emissions of chemical products have changed significantly in recent decades in an

64   effort to reduce the ozone (O_3) and secondary organic aerosol (SOA) formation potential (Weschler, 2009; CARB,

65   2015; Shin et al., 2016). For example, water-borne paints are increasingly replacing solvent-borne paints, while

66   simultaneously many VOC ingredients are being replaced with water (Matheson, 2002), "exempt" VOCs, or low-

67   vapor-pressure VOCs (LVP-VOCs) (Li et al., 2018). The California Air Resources Board (CARB) defines "exempt"

68   VOCs as compounds that are not expected to meaningfully contribute to ozone formation due to their low reactivity

69   in the atmosphere. Examples include acetone, ethane, perchloroethylene, methyl acetate, and

70   parachlorobenzotrifluoride (PCBTF). CARB also exempts several LVP-VOC, which are defined as chemical

71   compounds containing at least one carbon atom and a vapor pressure less than 0.1 mm Hg at 20°C, organic compounds

72   with more than 12 carbon atoms, compounds with boiling points greater than 216°C, chemical mixtures comprised

73   solely of compounds with more than 12 carbon atoms, or as the weight percent of a chemical mixture that boils above

74   216°C (Li et al., 2018). As a result of product reformulations and VOC exemptions, many paints can now be classified

as "zero VOC" paints that fall below the government-regulated permissible amounts, even though they emit compounds that are more broadly defined within the category of VOC. Compounds classified as intermediate-volatility and semi-volatile organic compounds (IVOCs and SVOCs) are often excluded from inventories and regulations due to measurement limitations or long emission time-scales, yet many are key SOA precursors that can be emitted by coating products or processes (Khare and Gentner, 2018).

Presented here are ambient and laboratory measurements of vapors emitted from coatings using a proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) to evaluate potential tracer compounds. PCBTF and Texanol will be shown to be detected at ambient levels, are VOCs emitted primarily by coatings products, and are unique VOCs prevalent in emissions inventories . Ambient measurements show the spatial and temporal trends of PCBTF and Texanol emissions in New York City (NYC), Chicago, Pittsburgh, and Denver. These ambient measurements are linked to coatings using a series of laboratory measurements sampling various architectural coatings. First, we compare VOC composition from coating headspace samples analyzed using PTR-ToF-MS with gas chromatograph (GC) pre-separation. These measurements highlight the differences in VOC composition for a variety of coating products and help to unambiguously identify VOC tracers linked to solvent and water-borne coatings. Emission factors (g kg^{-1}) of VOC mass are measured via controlled evaporation experiments to quantify key VOC emissions from coating use. Lastly, ingredient compilations from architectural coatings surveys from CARB are compared with the laboratory measurements to confirm usage trends. Coating surveys generally agree with the ambient and laboratory measurements and support the assignment of Texanol and PCBTF as atmospheric tracers for water-borne and solvent-borne coatings, respectively.

2 Experimental Methods

2.1. Instrumentation

2.1.1 PTR-ToF-MS

Mixing ratios of VOCs in ambient and laboratory measurements were determined using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS; referred to hereafter as PTR-ToF) (Yuan et al., 2016; Yuan et al., 2017). The PTR-ToF measures a large range of aromatics, alkenes, nitrogen-containing species, and oxygenated VOCs. Instrument backgrounds were determined for laboratory measurements before and after every experiment for short duration experiments, or every 2 h for longer duration experiments and ambient measurements, by passing air through a platinum catalyst heated to 350°C. Data were processed following the recommendations of Stark et al. (2015) using the Tofware package in Igor Pro (WaveMetrics). The PTR-ToF was calibrated using gravimetrically-prepared gas standards for typical water-borne solvents such as acetone and methyl ethyl ketone, and solvent-borne compounds such as toluene and C8-aromatics. Texanol and PCBTF were calibrated by liquid calibration methods as described by Coggon et al. (2018). The sensitivities for Texanol and PCBTF for 1 second measurements was were 9 and 69 normalized counts per second per ppbv (ncps ppbv^{-1}), respectively, and the detection limits for both were < 10 pptv (Gkatzelis et al. 2020a2021a). Texanol ($C_{12}H_{24}O_3$) was measured as a dehydrated fragment at m/z 199.169

183 $(C_{12}H_{22}O_2 \cdot H^+)$ and PCBTF $(C_7H_4ClF_3)$ was detected at m/z 160.996 $(C_7H_4ClF_2)$ from the loss of fluorine. The

184 sensitivity of compounds that were not calibrated were calculated according to Sekimoto et al. (2017).

185 The PTR-ToF is less sensitive to smaller hydrocarbons (de Gouw and Warneke, 2007; Sekimoto et al., 2017)

186 and substantially underestimates their mixing ratios. PTR-ToF sensitivities to alkanes and alkenes are typically only

187 a few percent of those for oxygenates (Warneke et al., 2003), and the sensitivities calculated using methods outlined

188 in (Sekimoto et al., 2017) are likely overestimated. Theoretical calibration factors from reaction rate coefficients have

189 been shown to be biased high for alkanes and alkenes (Warneke et al., 2003). In order to more accurately quantify the

190 contributions of hydrocarbons (HCs), the calculated sensitivities for low molecular weight HCs (< C5) were assumed

191 to have the same sensitivity as low molecular weight alkanes (10 ncps ppbv^{-1}). This results in an estimated uncertainty

192 in total VOC emissions of about a factor of two.

193

194 **2.1.2 GC Front End to PTR-ToF-MS**

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196 PTR-ToF-MS only resolves VOC molecular formulae. Gas chromatography (GC) pre-separation has been

197 used previously to identify structural isomers (Warneke et al., 2003; Koss et al., 2016). Here a custom-built GC

198 described by Kuster et al. (2004) was updated and re-designed specifically as a PTR-ToF-MS front end to analyze the

199 complex headspace mixture of select coating formulations. Details describing the setup and performance of the GC

200 interface are provided in the supplemental information and only a brief description is provided here.

201 The GC consists of a 30 m DB-624 column (Agilent Technologies, 30 m, 0.25 mm ID, 1.4 µm film thickness)

202 and oven combination identical to the system described by Lerner et al. (2017), a liquid nitrogen cryotrap, and a 2

203 position 10-port valve (VICI) to direct gas flows. The column was selected to measure polar and nonpolar VOCs in

204 the approximate range of C4C3-C10. The effluent of the GC column is injected into the PTR-ToF inlet. Depending

205 on the application, 1-5 minute samples can be collected and chromatogram lengths of 10-20 minutes can be chosen

206 such that the total run trapping and analysis time is between 15 and 30 minutes. LabVIEW (National Instruments)

207 software controls the sequence of events, hot and cold trap temperatures, valve switching, sample flow and carrier gas

208 flow. The detection limit for commonly detected VOCs (e.g., isoprene, benzene, xylenes) using this cryofocusing

209 system is ~ 5 pptv.

210

211 **2.2. Laboratory Measurements**

212 Laboratory measurements were performed to qualitatively evaluate the headspace VOCs emitted from commonly used

213 coatings. Nineteen different solvent- or water-borne formulas were tested, and ranged in applications including paints,

214 stains, primers, sealers, and preservatives. It is worth noting that industrial coatings formulated to withstand extreme

215 environmental conditions were not a part of this survey. The headspace VOCs were sampled by placing the product

216 container close to the PTR-ToF inlet and zero air was sampled between runs. The GC front end was used to aid the

217 specific identification of VOC isomers emitted from different coating types, which were compared to the ingredient

218 lists or CARB coating surveys.

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

229

230 **2.~~3~~2. Mobile and Ground-site Measurements**

231 The field measurements used to evaluate ambient measurements of coatings are described in detail by Coggon et al.

232 (~~2020~~2021) and Gkatzelis et al. (~~2020a~~2021a). Briefly, measurements were conducted during the New York

233 Investigation of Consumer Emissions (NY-ICE) campaign in winter (March 5 – 28, 2018) and the Long Island Sound

234 Tropospheric Ozone Study (LISTOS) in summer (July 5 – 24, 2018) to characterize the emission profile, strength, and

235 seasonality of VOCs emitted from VCPs.

236 Ground-site measurements were performed at the City College of New York (CCNY) campus. Mobile VOC

237 measurements were conducted throughout NYC and other urban regions (Pittsburgh, Chicago, and Denver) using the

238 NOAA Chemical Sciences Laboratory (CSL) mobile laboratory to characterize the spatial distribution of VCP

239 emissions. The mobile laboratory was driven through the boroughs of New York City, Long Island, and eastern New

240 Jersey, and multiple drives were performed in Chicago (2) and Denver (3). In each case, the mobile laboratory was

241 driven downwind, upwind, and through the city center to evaluate urban VOC enhancements. Drive routes were

242 selected to sample regions of both high and low population density to investigate differences in VCP emissions.

243

244 **2.~~4~~3. FIVE-VCP Emission Inventory**

245 The Fuel-based Inventory of Vehicle Emissions and Volatile Chemical Products (FIVE-VCP) emission inventory used

246 in this work was described in detail by Coggon et al. (~~2020~~2021). Briefly, VCP emissions were estimated from

247 chemical production data determined from a "bottom up" mass balance of the petrochemical industry. The VOC

248 speciation profiles were updated for the coatings category to include more recent architectural coating surveys by the

249 California Air Resources Board (CARB) (CARB, 2018). The per capita use of VCPs specific to the coating sector

250 was estimated and combined with VOC emission factors (in g VOC per kg product) reported by McDonald et al.

251 (2018a) that is based on a review of indoor air quality literature. The VCP emissions were spatially apportioned using

252 US Census block population data (Bureau USC, 2020a) and the temporal patterns are taken from the National

253 Emissions Inventory (NEI) 2014 (EPA, 2017).

254 Mobile source emissions are estimated utilizing a fuel-based approach based on fuel sale reports for on-road

255 and off-road engines. CO and VOC emission factors (in g VOC per kg fuel) were taken from the compilation by

293 McDonald et al. (2018a) and updated to 2018 by Coggon et al. (~~2020~~2021). The emission factors include tailpipe
294 emissions from running exhaust, enhanced emissions associated with cold-starting engines, and evaporative gasoline
295 VOC sources. The spatial and temporal emission patterns of mobile source engines are taken from the NEI 2014 (EPA,
296 2017).

297 **2.4. Laboratory Measurements**

298 Laboratory measurements were performed to qualitatively evaluate the headspace VOCs emitted from commonly used
299 coatings. Nineteen different solvent- or water-borne formulas were tested, and ranged in applications including paints,
300 stains, primers, sealers, and preservatives. It is worth noting that industrial maintenance coatings formulated to
301 withstand extreme environmental conditions were not a part of this survey. The variability in product formulation and
302 usage is significant and the coatings in this study were selected based on availability, total VOC content, and similarity
303 between other products tested, therefore the results do not fully capture the emissions variability of all coatings. Each
304 product was mixed thoroughly in its original container and an aliquot was transferred into a glass vial. The headspace
305 VOCs were sampled by placing the product container that was open to the atmosphere within a few centimeters of the
306 PTR-ToF inlet. The instrument inlet tubing was a short piece of PFA Teflon to limit losses or delays (Deming et al.,
307 2019). The container was closed between GC sample intervals (20 min) and zero air was sampled between runs. The
308 GC-front end was used to aid the specific identification of VOC isomers emitted from different coating types, which
309 were compared to the ingredient lists or CARB coating surveys.

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

320

321 **3 Ambient Measurements of PCBTF and Texanol**

322 The NYC ambient measurements of PCBTF and Texanol from ~~the ground site and~~ the mobile laboratory in 2018 are
323 summarized in Fig. 1. In Fig.1a, the drive tracks overlay a map of the population density in the region and are color
324 coded with summer-time PCBTF and Texanol. The population density is highest in Manhattan with more than 28,000
325 people km^{-2}. Generally, the highest mixing ratios of PCBTF and Texanol were found in the areas with the highest
326 population density, but were mostly dominated by short, spatially isolated plumes. The median mixing ratios of
327 PCBTF and Texanol were binned along the east-west transects together with the population density as shown in the
328 top panel. Multiple drives across the two seasons were conducted and longitudinally overlapping drives were averaged.
329 The correlations with population density for both compounds (R^2= 0.23 and 0.57) were lower than what was found

for most other VCP tracer compounds ($R^2 > 0.8$, Gkatzelis et al., ~~2020a~~2021a). This is consistent with PCBTF and Texanol being from construction activities, rather than correlated with population like other VCP tracers (e.g. D5 siloxane for personal care products). The mobile sampling strategy relied on either no or a relatively small number of repeat visits in both seasons and therefore does not represent long-term spatial patterns (Messier et al., 2018; Robinson et al., 2019), however, we might expect emissions from coatings to not show strong long-term spatial patterns as construction activities are generally not permanently located. In the lower panel, the time series from the ground site measurements in winter and summer for PCBTF and Texanol are shown together with CO, a combustion tracer, and D5 siloxane, a personal care product tracer (Coggon et al., 2018). At the end of the winter ground-site measurements in late March, a stagnation period, marked in Fig. 1b with the orange box, increased the mixing ratios of all VOCs and CO. The correlations with CO for the winter measurements are also shown in Fig. 1c. Throughout the entire campaign, the correlation of PCBTF and Texanol with CO is low, except for the time period at the end of March (orange) where the urban emissions of near-by sources accumulated at the measurement site. PCBTF and Texanol are also poorly correlated with D5 siloxane, except during the stagnation period ($R^2 = 0.50$ and $R^2 = 0.76$). This suggests that PCBTF and Texanol have sources other than combustion and personal care products and the large spikes in PCBTF observed during the drives shows that high emissions are from distinct point sources, and not from dispersed sources like traffic. Enhancements of PCBTF do not necessarily coincide with Texanol enhancements. The poor correlation between PCBTF and Texanol ($R^2 < 0.1$) is not unexpected since the primary source varies by product formulation and usage (e.g., water- or solvent-borne).

Even though PCBTF and Texanol have different sources than CO, the correlation with CO during the stagnation event can be used to estimate the PCBTF and Texanol emissions in NYC following the method described by Coggon et al. (~~2020~~2021), which uses the slope from the correlation together with CO emissions from the bottom-up FIVE mobile source inventory (McDonald et al., 2018b). The resulting emissions for PCBTF and Texanol in NYC were approximately 1 and 0.1 mg person^{-1} day^{-1}, respectively.

Figure 2~~a~~ summarizes the mobile laboratory measurements in Chicago, Pittsburgh, Denver, and the transit in between the cities, where the drive tracks close to the downtown areas in each city are color coded by PCBTF mixing ratio and plotted on top of the population density. Like NYC, PCBTF~~,~~ and Texanol were generally enhanced in urban regions, but not well correlated with urban population density. PCBTF was significantly enhanced in Chicago in distinct locations, and not well correlated with D5 siloxane (~~Fig. 2b,~~ $R^2 < 0.1$). The population density dependence of PCBTF and Texanol for winter and summer is shown in Fig. 3a as the ratio of the respective tracer with benzene, which is used as a tracer for mobile source emissions. This ratio controls for meteorology between cities, and also reflects differences in the proportion of VCP and traffic emissions across urban regions. As population density increases, mobile source emissions plateau because of roadway capacity and increased mass transit usage (Gately et al., 2015), while emissions from ~~VCPs~~ personal care products and other daily-use VCPs driven by human activity scale linearly with the number of people. Consequently, the ratio of a VCP markers (e.g. D5 siloxane) with benzene is higher in more densely populated regions (Gkatzelis et al., ~~2020a~~2021a). PCBTF and Texanol do not exhibit a population density dependence ($R^2 < 0.2$), especially compared to D5 siloxane ($R^2 = 0.82$) (Fig. 1 in Gkatzelis et al. (~~2020a~~2021a)), which likely indicates that emissions from coatings are influenced by industrial usage patterns, such

as construction or manufacturing activity, rather than consumer product usage patterns, which impact the spatial and
temporal variability of D5 siloxane (Coggon et al., 2018; Coggon et al., 2018; Gkatzelis et al., ~~2020a~~2021a).

The weekly profiles of the PCBTF and Texanol ratios for summer and winter NYC ground site
measurements are shown in Fig. 3b. Winter ratios are lower than those in summer, which likely indicates a seasonal
change in emissions due to relatively fewer coating projects in the wintertime. The same was observed in the other
cities as can be seen in Fig. 3a, where the winter data show a much smaller correlation with the population density
compared to summer. In addition to usage trends, it is also likely meteorology accounts for some of changes in
emissions between seasons and further complicates interpretation. Texanol ($C_{12}H_{24}O_3$) is detected as a fragment at m/z
199 ($C_{12}H_{22}O_2$). It has been suggested that compounds formed via chemical processes are a potential interference at
that mass during summer months (Gkatzelis et al., ~~2020a~~2021a). A PMF analysis of the ambient dataset used herein
is described in detail in Gkatzelis et al. (~~2020b~~2021b) and noted that the majority of m/z 199 was attributed to the VCP
emissions in summer NYC (>60%), while the remaining fraction was attributed to daytime/morning chemical
processes influenced by VOC oxidation. Therefore, photochemistry might contribute to the larger Texanol ratio
observed in summer compared to winter and complicates the use of PTR-ToF measured Texanol as a tracer for paints
during summer months. Nevertheless, Goliff et al. (2012) observed the highest mean ambient concentrations of
Texanol from sorbent-tube collection during summer months in multiple cities, which are unaffected by interferences
to other compounds. It might also be expected that coatings emissions are smaller on the weekends compared to
weekdays, but this difference is not clearly observed in Fig. 3b. Currently, the FIVE-VCP does not take the seasonality
of VCP emissions into account and therefore likely overestimate coatings emissions during winter.

4 Headspace and Evaporation Measurements

Gkatzelis et al. (~~2020a~~2021a) used the population density dependence of various VOCs to identify specific tracers for
VCP emissions. Although PCBTF and Texanol ambient mixing ratios did not show a strong population dependence,
they met additional criteria for selection as VCP tracers, i.e., they were regularly measured at significant mixing ratios
in ambient air and are uniquely represented in the FIVE-VCP emission inventory as a component of coatings. To
demonstrate the prevalence and efficacy of these compounds as markers in the coating VCP category, laboratory
measurements were performed to sample VOCs from the headspaces of commonly used architectural coatings and to
quantify the fraction of PCBTF and Texanol associated with the measured VOC mass.

To understand the composition of the emissions from coating products in greater detail, the vapors from the
headspace of nineteen different coatings were measured by PTR-ToF. To capture the two ends of the spectrum, both
a water-borne "zero VOC" low odor paint and a solvent-borne polyurethane stain were tested with the GC-front end
pre-separation method described above (GC-PTR-ToF-MS). The GC-PTR-ToF-MS chromatograms of select (a) small
oxygenates, (b) hydrocarbons (HC), and (c) aromatics are shown in Fig. 4. For the "zero VOC" paint, the main
oxygenate emitted was acetone, with smaller emissions from other solvents including methanol, ethanol, and
methylethylketone (MEK). The compounds identified in the "zero VOC" GC hydrocarbon panel are primarily
fragments of oxygenated compounds and, generally, oxygenated compounds were the dominant emission from "zero
VOC" paint. Emissions from aromatics were negligible. The mass for Texanol and its fragments were observed in the

direct PTR-ToF sampling of the headspace of several water-borne products, but pure Texanol injections into the GC-PTR-ToF-MS demonstrated that Texanol does not elute from the GC column either because it is lost to the water trap or has too low of a vapor pressure to elute from the column under the selected temperature program. As a stand-alone instrument, the PTR-ToF-MS has the distinct advantage of having a rapid sampling time (~0.1-5 seconds). The GC-inlet system requires ~10-15 minutes for the sequence of sample preconcentration, injection, GC separation, and detection. It was originally developed to collect a sample in the GC during sampling with the PTR-ToF-MS followed by interrupting normal sampling to analyze the chromatogram and take advantage of chromatographic separation. This setup still maintains >75% of the time dedicated to in-situ PTR-ToF sampling. The GC system is capable of detecting C3-C10 compounds and development included calibration standards in that range, which keeps the sampling and analysis times relatively short while capturing the majority of typical VOCs observed in ambient air. Further characterization of larger and less volatile compounds such as Texanol would have required a different GC system with significantly longer cycle times.

The GC peaks of the solvent-borne polyurethane in the chromatograms were several orders of magnitude larger than those for the water-borne product. Acetone and MEK were the most abundant small oxygenates, while ethanol and methanol emissions were negligible. Over 30 distinct hydrocarbon peaks were detected with retention times over 300s and with mass 55 ($C_4H_6 \cdot H^+$) and mass 69 ($C_5H_8 \cdot H^+$) dominating, which indicates C4- and larger hydrocarbons as the primary constituents. Stoddard solvent is commonly listed as an ingredient in solvent-borne coatings, and mainly consists of < C10 alkanes, cycloalkanes, and aromatics (Censullo et al., 2002), which are clearly evident in the mass spectrum. These hydrocarbons are likely not useful unique tracers for coatings products due to overlapping contributions from gasoline and diesel fuel emission in urban areas (Gentner et al., 2012; Gentner et al., 2013), and therefore a detailed discussion of all the hydrocarbon peaks is beyond the scope of this work. Benzene (*m/z* 79) is one of the aromatics with minor emissions, but most other C7-C12 aromatics including toluene (*m/z* 93) were more significant. Benzene is often reduced in coating formulations due to its toxicity. The largest aromatic peak is PCBTF, which is completely absent in all water-borne products that were tested.

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

478 The "zero VOC", low odor paint and the primer/sealer paint have relatively low emissions, which were

479 dominated by small oxygenated VOCs (methanol, ethanol, formaldehyde, and acetone). The primer/sealer paint also

480 emitted Texanol, which can be expected from the ingredients of many water-borne products. The Texanol signal

481 measured in the laboratory experiments has no contribution from the oxidation products that were identified as

482 potential interferences during ambient summer sampling (Gkatzelis et al., 202~~0~~1a; Gkatzelis et al., ~~2020b~~2021b).

483 Methanol, ethanol, and acetone emissions are expected ingredients, as listed in the FIVE-VCP inventory.

484 Formaldehyde is not an ingredient, but emissions might be expected from the use of preservatives that include

485 formaldehyde-condensate compounds that rely on the release of free formaldehyde from the hydrolysis of a parent

486 structure such as dimethylol glycol and dimethylol urea. Dimethylol glycol and dimethylol urea are routinely used as

487 biocides in water-borne paints and fungicidal products, but have now been widely replaced by other compounds such

488 as isothiazolinones (Salthammer et al., 2010). Ethylene glycol is an abundant ingredient in architectural coatings sales

489 surveys (CARB, 2018), and has been observed in an indoor air study during a painting event (Pagonis et al., 2019).

490 The signal at mass 45 ($C_2H_4O \cdot H^+$) is typically attributed in PTR-MS studies to acetaldehyde (de Gouw and Warneke,

491 2007), but ethylene glycol fragments mostly to m/z 45. Acetaldehyde was present in the GC experiments and although

492 ethylene glycol was not observed, as it is likely lost in the water trap, its dominance in architectural coatings and paints

493 suggests it may be a dominant species at that mass.

494 The total VOC signal was significantly larger by an order of magnitude for water-borne latex paint than for

495 the two other water-borne paint products, with ethanol being the biggest emission. In addition to the small oxygenated

496 VOCs, larger compounds such as dipropylene glycol monobutylether and other ketones and acetates were emitted.

497 Several species listed as ingredients in CARB coatings surveys were tentatively identified in the paint emissions as

498 ethylene glycol, methyl-n-amyl ketone, 1-methyl-2-pyrrolidinone, and methyl-, vinyl-, ethyl-, and butyl acetate. For

499 butyl acetate, the major peak in the GC chromatogram at mass 117 correlated strongly with peaks at m/z 61 and 43,

500 which are known fragments of the parent ion (Buhr et al., 2002).

501 As was expected from the GC analysis, the VOC emissions of the solvent-borne polyurethane were markedly

502 different and ~5 times larger than the water-borne paint. Hydrocarbons and aromatics are clearly evident in the mass

503 spectrum. Small masses (C<5) are known to be affected by fragmentation, which adds to quantification uncertainty,

504 and most hydrocarbon masses had multiple peaks in the GC chromatograms. As was noted in the headspace GC

505 experiments, the solvent-borne polyurethane also emitted PCBTF.

506 The weight loss recorded on the scale during the evaporation experiments equals the mass emitted as VOCs,

507 water (which was not measured), and other compounds undetectable by PTR-ToF. Each measured VOC (mg m^{-3}) was

508 converted to an emission rate (mg s^{-1}) by multiplying with the gas flow rate and integrated across the length of the

509 experiment to determine the total mass emitted by each individual species. Figure 6 shows the time series of mass

510 emitted as the sum of all measured VOCs overlaid with the weight change measured on the Teflon covered scale for

511 each evaporation experiment.

512 For the water-borne products in Fig. 6a-c, the mass emitted as VOCs is a very small fraction of the mass lost

513 from the coatings product (<1 to 7%) and the main weight loss is attributed to water. Fig. 6b shows the time series for

514 the primer/sealer paint, which was the product with the largest difference in VOC emission rate and mass lost. This

552   mass loss rate gradually leveled off, while the total VOC emission continued to increase at a steady rate. This was

553   largely driven by only a few compounds (e.g. ethylene glycol), and therefore the estimated mass loss and emission

554   factors reported herein represent lower-end estimates. Latex paint showed a similar behavior with VOCs steadily

555   rising even at the conclusion of the experiment. These results are not unexpected, as emissions of Texanol from paints

556   have been observed for periods as long as 15 months (Lin and Corsi, 2007) and these experiments were stopped after

557   19 hours. The VOC mass emitted, as detected by PTR-ToF, is related to the VOC content of the product, where the

558   latex paint clearly has the largest VOC emission and the "zero VOC" paint the lowest.

559   For the solvent-borne polyurethane coating in Fig. 6d, the mass emitted as VOCs exhibited a temporal profile

560   that more closely mirrored the mass lost recorded by the scale. The similarity in the emission profile and weight loss

561   indicate that the majority of the weight loss from the solvent-borne stain is due to VOC emissions with only a small

562   fraction of weight loss from other undetected compounds or underestimation due to poor sensitivity to hydrocarbons.

563   The mass remaining on the scale indicated that about 40% of the weight remained as solids or unevaporated VOCs,

564   which is within 5% of what is expected from the manufacturer reported VOC content of 550 g L^{-1}. Figures 6b and 6d

565   represent two extremes and it is likely each product will have different evaporative properties depending on the overall

566   composition and atmospheric conditions. Figure 6 also shows that for the (a) "zero VOC" paint and (d) polyurethane

567   stain, the VOCs emitted in the first hour account for over 50% of the total mass emitted as measured VOCs over the

568   course of this experiment. Latex paint (c) takes an additional hour and the primer/sealer (b) takes nearly 6 hours for

569   the majority of the measured VOCs to evaporate. The experiment did not complete to dryness, thus the total mass

570   measured is likely an underestimate, and potentially under-account semi- and intermediate-volatility VOCs that have

571   a lower volatility. Continued emissions from dry-paint have been observed following complete water evaporation

572   (Clausen, et al., 1991; Hodgson et al., 2000), though emissions from the dry-film were not investigated here.

573   Figure 7a shows the time series of the emission rates of the sum of all measured VOCs for each product (mg

574   h^{-1}). The solvent-borne polyurethane had a maximum VOC emission rate (6.7 mg h^{-1}) that was more than a factor of

575   two greater than the highest-emitting water-borne coating. For each product, the highest total VOC emission rate

576   peaked within the first 6 minutes. The elapsed time to reach the maximum emission rate varied to within a few minutes,

577   and this likely reflects the different volatilities of the ingredients. For the coatings tested here, the majority of the

578   measured VOC mass is emitted within the first few hours, and therefore the most significant atmospheric implications

579   for ozone formation likely occur during and shortly following application.

580   Figure 7b shows the relative contribution of select VOCs to the total VOC mass as a function of time during

581   the evaporation of the primer/sealer paint. Emissions of methanol and 1-butanol fragments dominated at the start of

582   the experiment, followed by other species including ethylene glycol and Texanol, which all peaked in a sequence that

583   paralleled reported saturation vapor concentrations (NIST Chemistry WebBook). The volatilities of candidate species

584   at mass 45 suggest ethylene glycol ($C_0 \sim 10^5$ µg m^{-3}) is the dominant compound, since the emissions of acetaldehyde

585   ($C_0 \sim 10^9$ µg m^{-3}) would have peaked before methanol ($C_0 \sim 10^8$ µg m^{-3}). The emissions of acetone and formaldehyde

586   are more complicated. Although the reported saturation vapor pressures are higher than methanol the maximum

587   emission rate peaked later and changed more gradually, resulting in more prolonged emissions. Fragmentation of

588   larger compounds with a range of volatilities, including glycols, to the *m/z* of acetone and formaldehyde is one possible

589 explanation for these discrepancies. It is clear that the contribution of specific compounds to the total mass emitted

590 can vary significantly over time and likely depends on volatility (C_0), the initial composition of the product, and other

591 factors such as drying time, temperature, humidity, and substrate interaction/properties. Texanol has a lower saturation

592 vapor concentration (10^5 µg m^{-3}), and the maximum emission rate occurred ~11 minutes into the experiment, but the

593 amount of mass emitted as Texanol during the first hour only accounted for 34% of the total Texanol emitted during

594 the entire experiment (~19 h). It took over 6 hours to account for 75% of the total emitted Texanol, demonstrating that

595 certain species can emit considerably across several hours to days. The majority of the Texanol emission does occur

596 within the first several hours, and the fast evaporation supports its use as a tracer. Lin and Corsi (2007) showed

597 emissions of Texanol decreased by 90% within the first 100 h following paint application, and mass closure

598 assessments showed that airborne emissions of Texanol were greater than recovery from material components for

599 thin-film flat paints. The VOC speciation in each evaporation experiment is shown in Fig. 5b.

600 The PTR-ToF also detects several inorganic species such as ammonia, though the signal at *m/z* 18 suffers

601 from high background signal and has only been quantified for large emission sources such as biomass burning (Karl

602 et al., 2007; Müller et al., 2014; Koss et al., 2018). There was a clear enhancement of ammonia in all water-borne

603 coatings that was absent in the solvent-borne coatings, and it is likely mass emitted as ammonia can be important in

604 water-borne products as it is commonly used as a pH stabilizer. The ammonia PTR-ToF sensitivity derived from a

605 comparison with an FTIR during biomass burning sampling (Koss et al., 2018) was used to estimate the mass emitted

606 as ammonia for the latex paint. The total mass emitted as ammonia (2.1 mg) rivaled the VOC mass (2.3 mg), and

607 shows ammonia emissions can be significant from certain water-borne products. There was no direct calibration of

608 ammonia during these experiments and therefore the discussion focuses on VOCs only.

609 Table 1 summarizes the results of the evaporation experiments. As expected, the solvent-borne polyurethane

610 VOC emissions accounted for the greatest amount of total mass detected (83%), which is likely a lower limit estimate

611 since the PTR-ToF is less sensitive to hydrocarbons. The trend in the VOC emissions qualitatively tracks the VOC

612 content reported on the product labels (g L^{-1}). The "zero VOC" paint data sheet reported < 5 g L^{-1} VOCs and emitted

613 very few VOCs with an emission factor (in g VOC emitted per initial weight of the product) of 0.7 g VOC kg^{-1} paint,

614 followed by the primer/sealer (2.8 g kg^{-1}), latex paint (43.1 g kg^{-1}), and finally polyurethane (495 g kg^{-1}) with a reported

615 VOC content of < 550 g L^{-1}. We note that the emission factors are underestimated since the experiments did not

616 complete to dryness. The actual density of each product would need to be known to calculate the VOC mass emitted

617 from the content labels, thus the comparisons described above are qualitative. The VOC emission rates for each

618 product, averaged during the 19-hour experiments, also mirror the VOC content. ~~We note that the emission factors~~

619 ~~are underestimated since the experiments did not complete to dryness.~~

620

621 **5 CARB Architectural Coatings Survey Data**

622 Every four to five years, CARB conducts comprehensive surveys of architectural coatings sold in California to gather

623 information about the ingredients and sales with the goal of updating emission inventories. The response to the surveys

624 is mandatory and CARB ensures the validity of the data following extensive quality assurance and quality control

625 measures and the results accurately represent the sales volume in California. The data are publicly available (CARB,

626 2018). Speciation is based on reported product formulations and emissions data reflect applicable fate and transport

627 adjustments.

628 Figure 8a shows the trend in sales and emission estimates for the last five surveys from 1990 to 2014. The

629 sales volume increased significantly from 1990 to 2004, but was lower in 2014 as the industry was still recovering

630 from the economic recession in 2007-2009 that led to a sharp decline in construction spending (Bureau USC, 2020b).

631 During this time, coating emissions continuously decreased from 126 tons/day to < 27 tons/day in California. Most of

632 the sale volume was associated with water-borne coatings, and the fraction increased ~~to~~ from ~ 75% of the total in

633 1990 to ~ 93% in 2013. The emissions, on the other hand, were dominated by solvent-borne coatings with > 72% of

634 the total in 1990 and half solvent-borne and water-borne each in 2014. This shows that the VOC content, and therefore

635 the emissions, of coatings in total have significantly decreased since the 1990s. Furthermore, the higher-emitting

636 solvent borne coatings are increasingly being replaced by water-borne products, which together resulted in this

637 significant emission reduction. The CARB survey also separates the sale and emissions into the different product

638 categories (not shown). Common water-borne paints, such as flat or low-gloss coatings and the accompanying primer,

639 make up the bulk of the total sales, but only about half of the emissions. In contrast, solvent-borne products such as

640 stains, varnishes, or rust preventative coatings are sold in lower volumes, but contribute the other half of the coating

641 emissions.

642 The South Coast Air Quality Management District (SCAQMD) also reports data from coatings sales and

643 emissions from 2008 to 2017 (reproduced in Fig. 8b). These data are part of the CARB survey and represent half of

644 the California-wide emissions. The sales in SCAQMD have been relatively steady ranging from 35-42 million gallons

645 with only slight increases since 2009, while the emissions have decreased significantly from 2008 to 2014 and were

646 constant around 11 tons/day from 2014 until 2017. This data set extends the CARB surveys and might indicate that

647 the overall emissions have not continued the steep decease after 2014, so that 2014 CARB data might still be

648 representative of the 2018 ambient measurements presented above.

649 The VOC ingredients of coatings reported in the CARB surveys have also changed significantly from 2005

650 to 2014. The left panels of Fig. 9a show the top 35 non-exempt VOC ingredients out of over 300 in the survey, together

651 with the exempt ingredients for 2005 and 2014 in the right panel. As was already clear from Fig. 8, the total amount

652 of VOC ingredients significantly decreased from 73 million pounds in 2005 to 23.6 million pounds in 2014, but also

653 the composition has changed. For example, in 2005 xylene was still a major ingredient of coatings but does not show

654 up in the top 35 ingredients in 2014. Even though the total amount of exempt ingredients stayed almost constant, the

655 relative amount has increased to almost 20% in 2014 from about 7% in 2005. The hydrocarbons from solvents are

656 generally the largest emissions, but small oxygenated VOCs, such as ethylene glycol, propylene glycol, acetone, and

657 ethanol, are also strongly emitted by paints and coatings and were detected as significant emitters in the laboratory

658 experiments. The ingredients measured as emissions in the ambient or laboratory experiments by the PTR-ToF are

659 indicated as solid bars in Fig. 9a for the 2014 data.

660 Most of the VOC ingredients shown in Fig. 9a are not unique to coatings products, but Texanol and PCBTF

661 are two compounds that are used only in coatings products as can be seen in Fig. 9b, where the fractions of VCP

662 emissions in the coatings category of various VOCs are shown. The compounds are sorted by their contribution to the

663   coatings category according to the FIVE-VCP inventory calculated using the method of McDonald et al. (2018a). The

664   only other compound besides Texanol and PCBTF that is predominantly attributed to coatings in the FIVE-VCP is

665   methylene chloride, but the amount used is too small to be a useful atmospheric tracer.

666   All the VOC ingredients collected by the CARB survey might not necessarily be emitted by the products; for

667   example Texanol airborne recoveries were between 25-90% depending on the paint and the substrate (Lin and Corsi,

668   2007) and in addition reactions and polymerization will occur in the production of the chemical products. The

669   ingredients that have been detected in either the evaporation experiments or the ambient measurements with the PTR-

670   ToF are indicated as solid bars for the 2014 data in Fig. 9a. Texanol emitted during evaporation of the primer/sealer

671   paint accounted for 13% of the measured VOC emissions. The ingredients reported in the CARB 2014 survey indicate

672   Texanol was 10% of the total VOC ingredient sales including exempt VOCs. The agreement between the laboratory

673   measurement of Texanol and the ingredients summary is reasonable considering the range in airborne recoveries.

674   PCBTF in the solvent-borne polyurethane only accounted for 0.2% of the total VOC mass as compared to the reported

675   ingredient sales contribution of 9%. These results demonstrate the challenges in generating a representative emissions

676   inventory from product sales as each product has a unique composition and ingredient sales do not necessarily equal

677   emissions. It is also possible that uses of PCBTF could differ between formulations available to consumers and those

678   used for professional ~~industrial~~ applications. Only a small selection of commercially available coatings were tested

679   here.

680   More details of the use of PCBTF and Texanol are shown in Fig. 10, where panel (b) shows that the use of

681   Texanol has strongly declined, while the use of PCBTF has increased such that they had comparable ingredients sales

682   in 2014. Both were around 10% of the total sale each. The pie charts in Fig. 10a show that PCBTF is mainly used as

683   a solvent in solvent-borne products, such as sealers, stains and polyurethane finishers. Texanol is used in water-borne

684   products as a coalescent for latex and other paints (Lin and Corsi, 2007). In summary, the CARB survey results in

685   Fig. 8, 9, and 10 indicate that PCBTF might be a good atmospheric tracer for solvent-borne coatings and Texanol for

686   water-borne coatings, even though the use of Texanol is rapidly declining.

687

688   **6 Conclusion**

689   Mobile field measurements in urban areas show that compounds largely associated with architectural coatings, such

690   as PCBTF and Texanol, were observed from point source locations near and around construction activity. Unlike other

691   VCP emissions previously described by Gkatzelis et al. (~~2020a~~2021a), these molecules do not correlate strongly with

692   population density, which suggests that their emissions are not driven by wide-spread, individual usage. In contrast,

693   the spatial and temporal patterns suggest that coating emissions are from discrete ~~industrial~~ applications, such as

694   architectural and construction projects.

695   Headspace analysis measured with a PTR-ToF and GC front end confirmed the identity of many VOCs

696   cataloged as ingredients in inventories compiled by CARB from architectural coating surveys. The "zero VOC" paint

697   analyzed had low VOC emissions dominated by small oxygenates including methanol, ethanol, and acetone, with

698   negligible emissions from smaller hydrocarbons and aromatics. The solvent-borne polyurethane stain emissions were

699   compositionally different with the distribution shifted largely towards hydrocarbons and aromatics with a clear

enhancement of PCBTF. The emission rates (mg s^{-1}) were calculated for each VOC and the total mass emitted as VOCs was calculated for the length of a controlled evaporation experiment and compared to total product mass emitted. The VOCs accounted for a range of 0.2-83% of the total mass emitted with the relative contribution mirroring the VOC content (g L^{-1}) reported by the manufacturer. Inorganic species such as ammonia were detected in water-borne coatings and likely contribute to some evaporative mass loss, though their contribution was not quantified in this study. The total VOC emission rates were highest within the first 6 minutes of application and for three of the four products, over 50% of the total VOC mass was emitted within the first two hours. These results highlight the importance of the initial evaporative emissions of coatings following application events, as they likely have important impacts on ozone.

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

Funding: CES, MMC, GIG, JO, BCM, JP, KA JBG, MT, and CW acknowledge the CIRES Innovative Research Program and NOAA Cooperative Institute Agreement (NA17OAR4320101).

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

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

Competing Interests
The authors declare that they have no conflict of interest.

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

Acknowledgements
The authors thank William Kuster for valuable conversations and assistance with the GC inlet system.

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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

889
890 **Table 1: Summary of the evaporation experiments for four coating types including percentage of mass lost as measured**
891 **VOCs (%), VOC emission factors (g kg^{-1} paint), reported product label VOC content (g L^{-1}), and the average and maximum**
892 **total VOC emission rates. Note: emission factors are lower-end estimates calculated based on the length of these experiments**
893
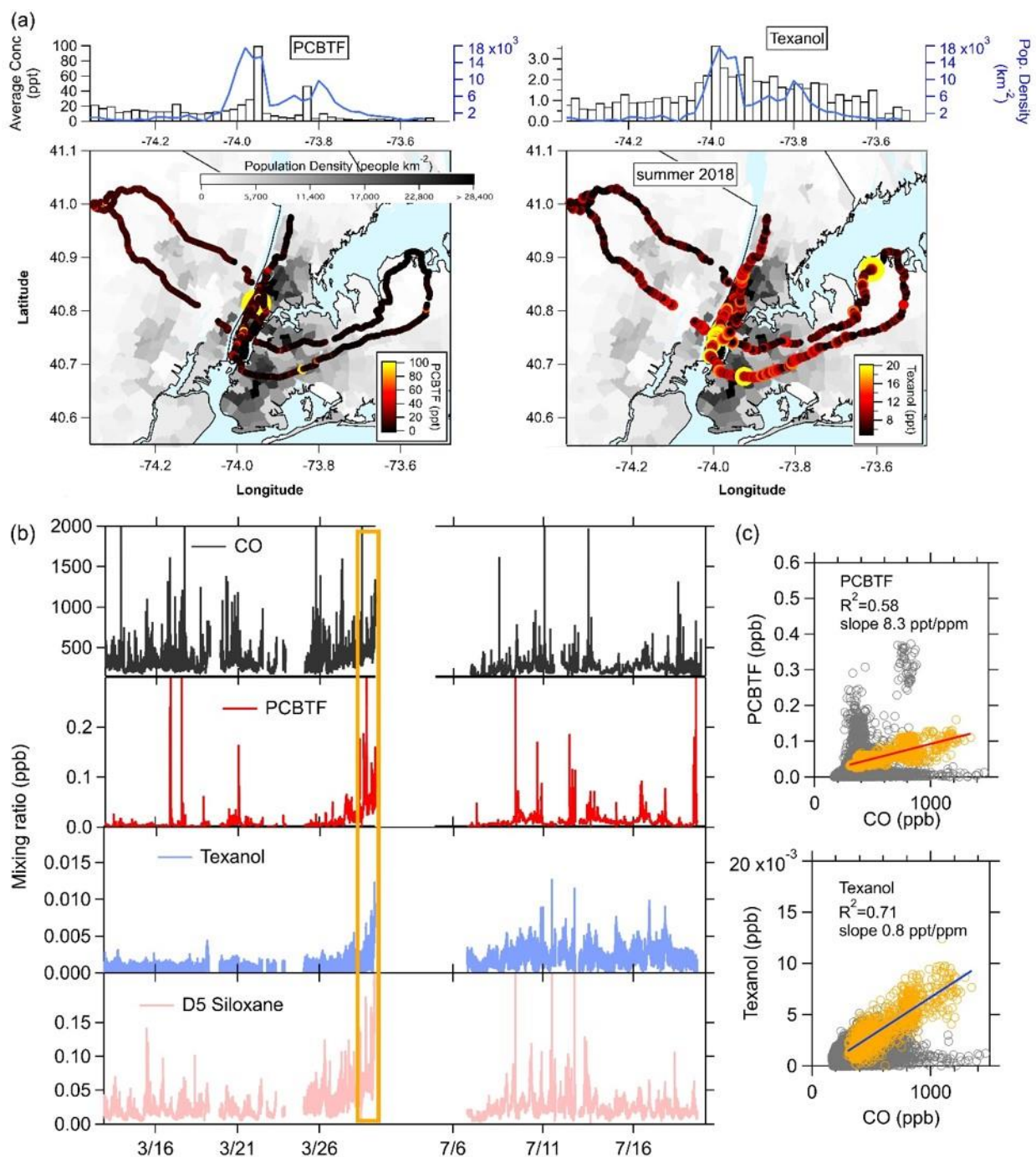
Figure 1: Summary of the PCBTF and Texanol measurements in New York City: (Map) Color-coded NOAA Mobile Laboratory drive track on a map of the population density. (a) Binned population density and mixing ratios. (b) Time series of CO, PCBTF, Texanol, and D5 siloxane for winter and summer months. The 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).
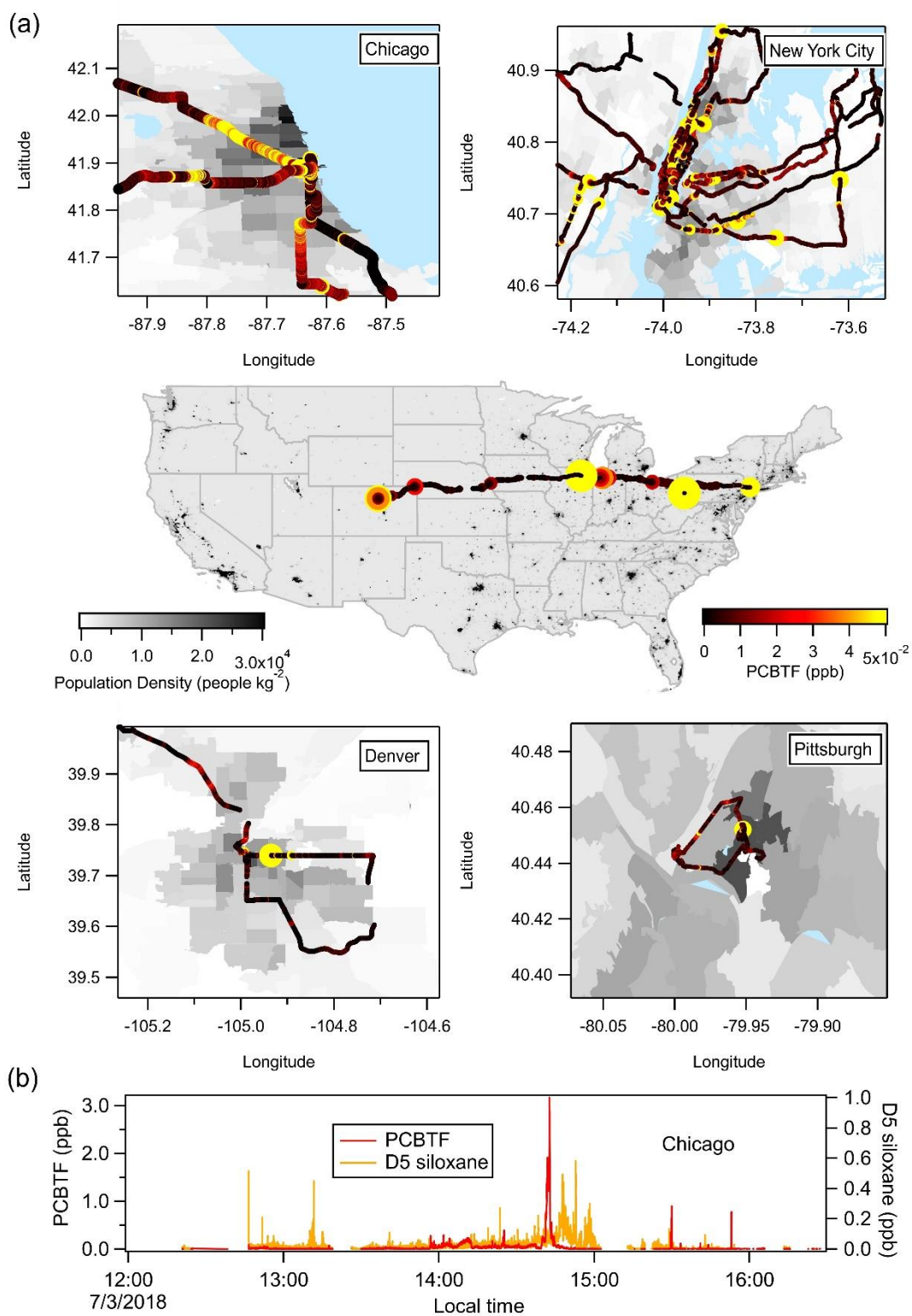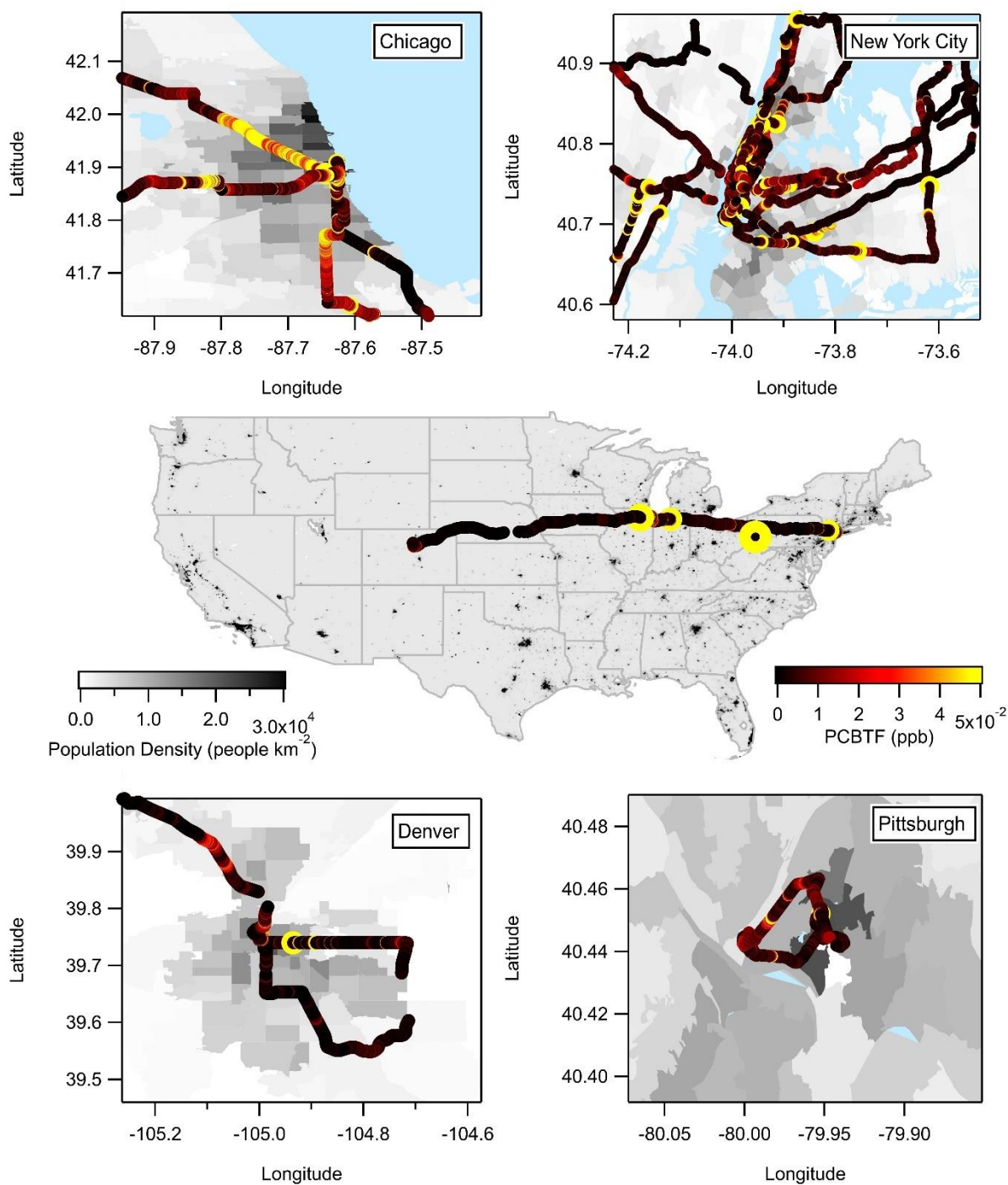
Figure 2: ~~(a)~~ Summary of the PCBTF ~~and Texanol~~ measurements from Chicago, New York City, Denver, ~~and~~ Pittsburgh, and the transition drives between the cities. ~~(b) Time series of PCBTF and D5 siloxane during Chicago drives.~~
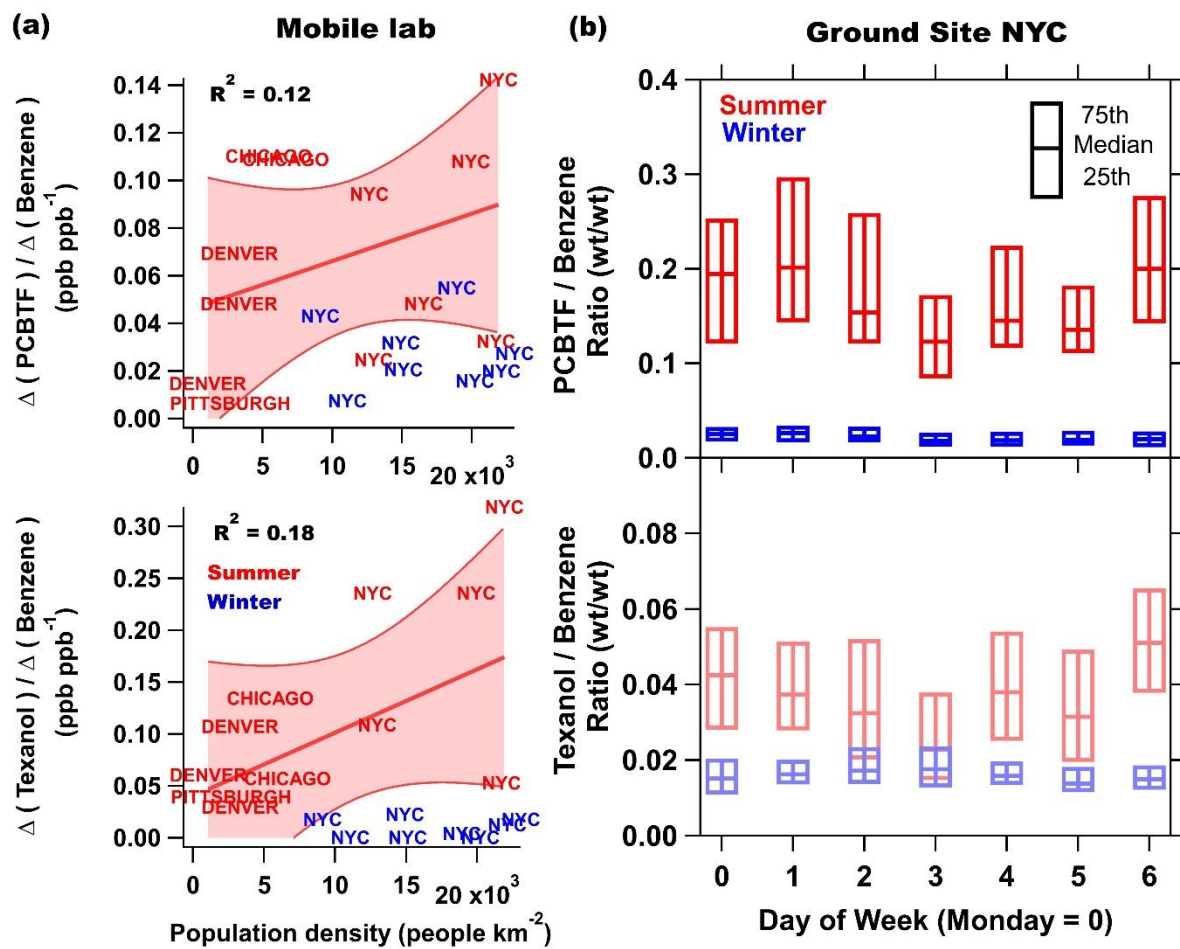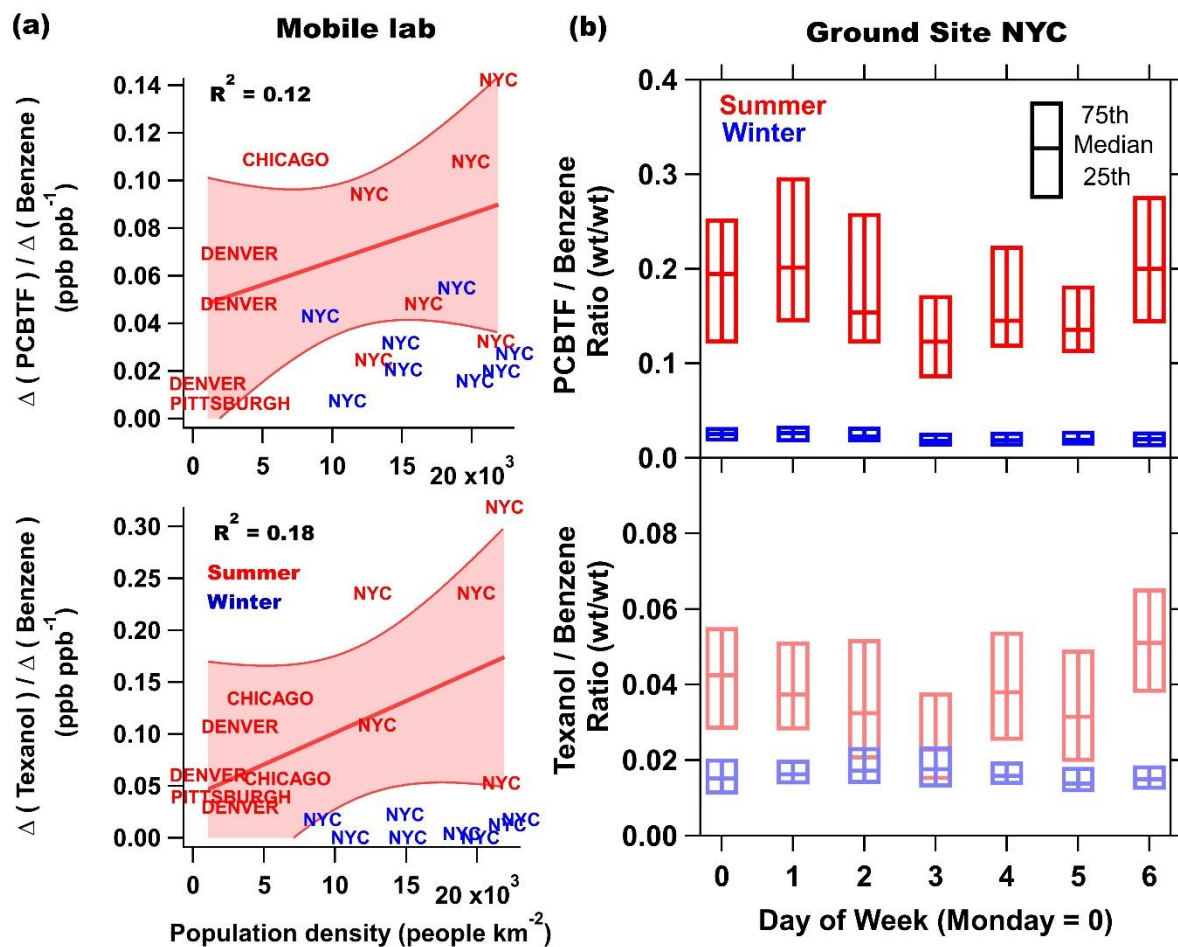
Figure 3: (a) The enhancement of PCBTF and Texanol relative to the enhancement of benzene versus the population density in summer (red) and winter (blue) in various cities. **Enhancements were calculated by subtracting the background median taken from measurements upwind of cities with the lowest mixing ratios from median concentrations from regions where population density was the highest.** 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.
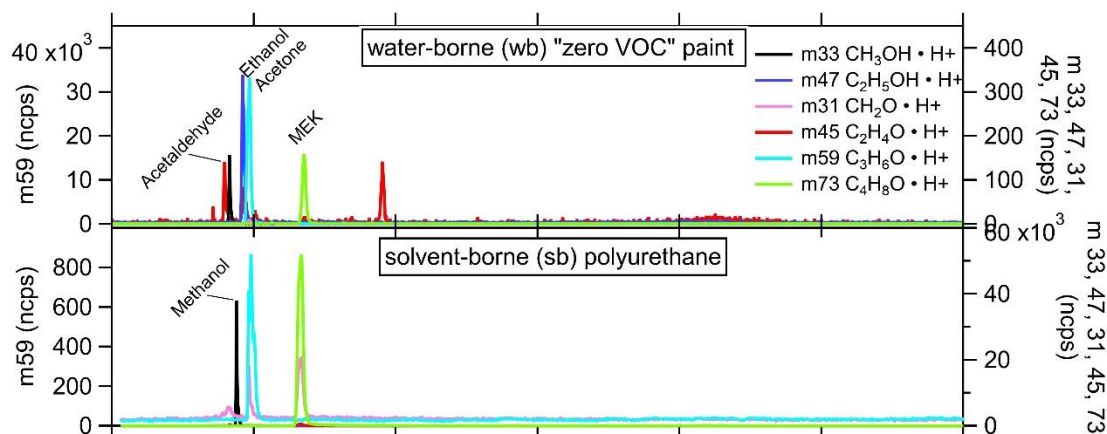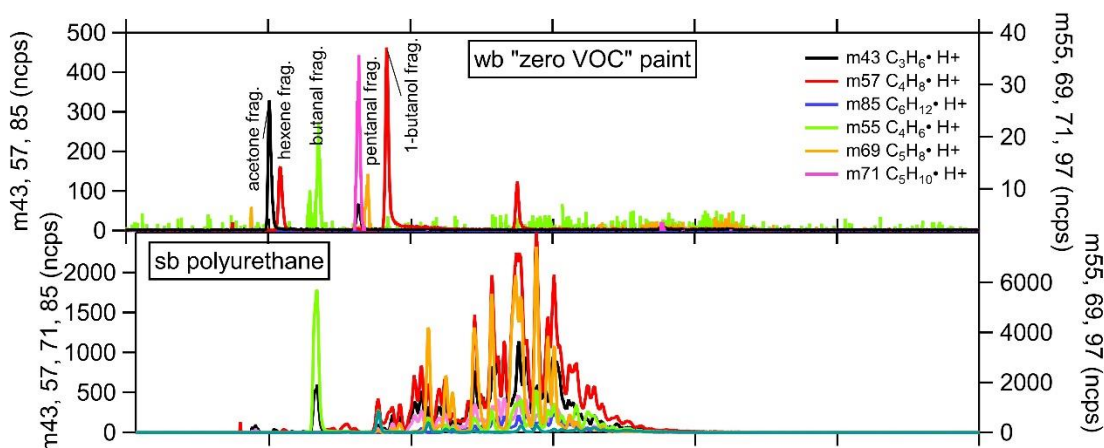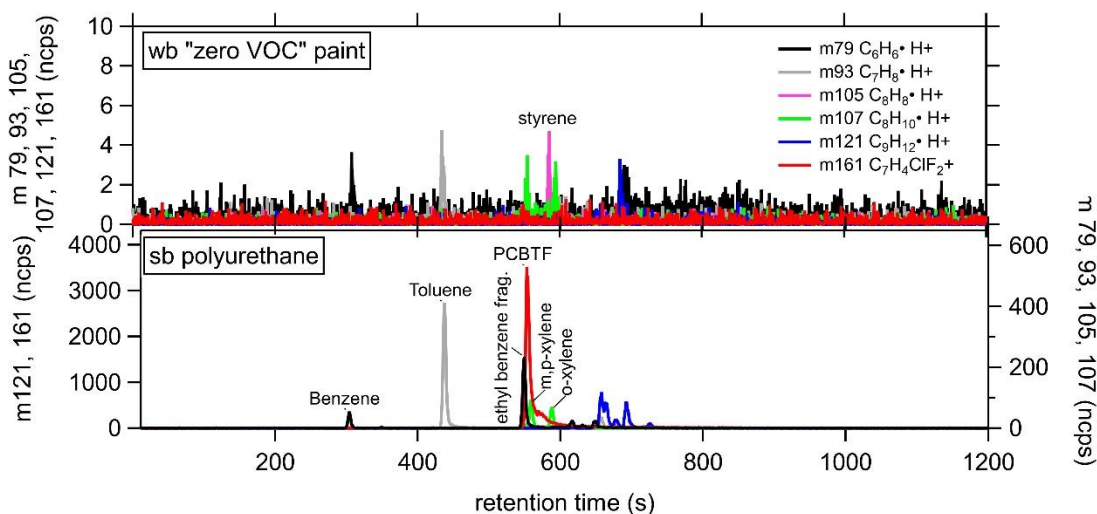
Figure 4: GC-PTR-ToF chromatogram from the headspace of a water-borne (wb), "zero VOC" low odor paint with ink and a solvent-borne (sb) polyurethane stain for (a) small oxygenates, (b) hydrocarbons, and (c) aromatics.

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 _taken from the early mass scan_ 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.
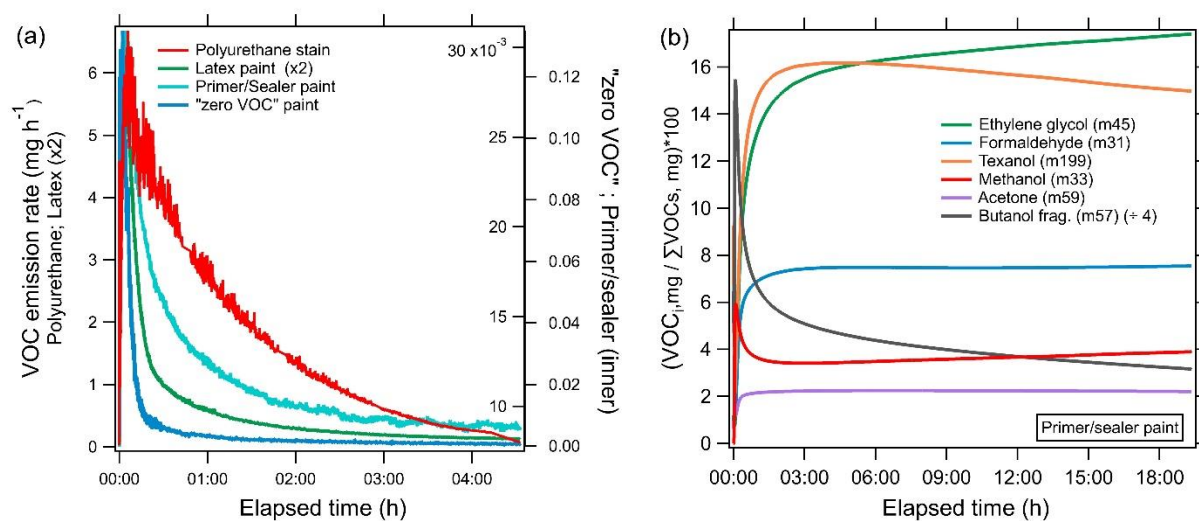
Figure 7: (a) Emission rates (mg h^{-1}) of all measured VOCs summed during evaporation experiments of different coating types: polyurethane stain (red), latex paint (green), primer/sealer paint (cyan), "zero VOC" paint (blue). (b) Time series showing the percent of integrated mass emitted as an individual VOC (VOC$_i$) to the total measured integrated 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.
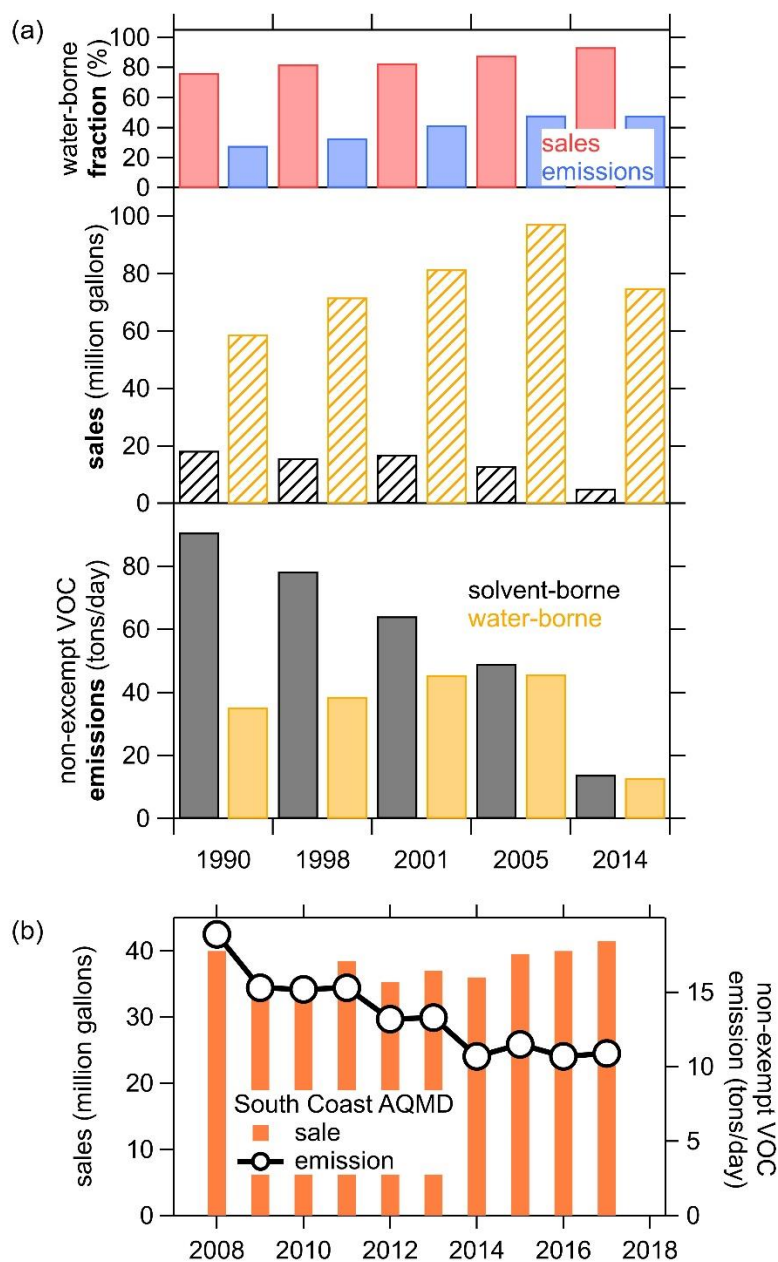
Figure 8: (a) Trends in paints and coatings sales and VOC emissions from the CARB coating surveys since 1990. (b) South Coast AQMD trend of coatings reproduced from: http://www.aqmd.gov/home/rules-compliance/compliance/vocs/architectural-coatings
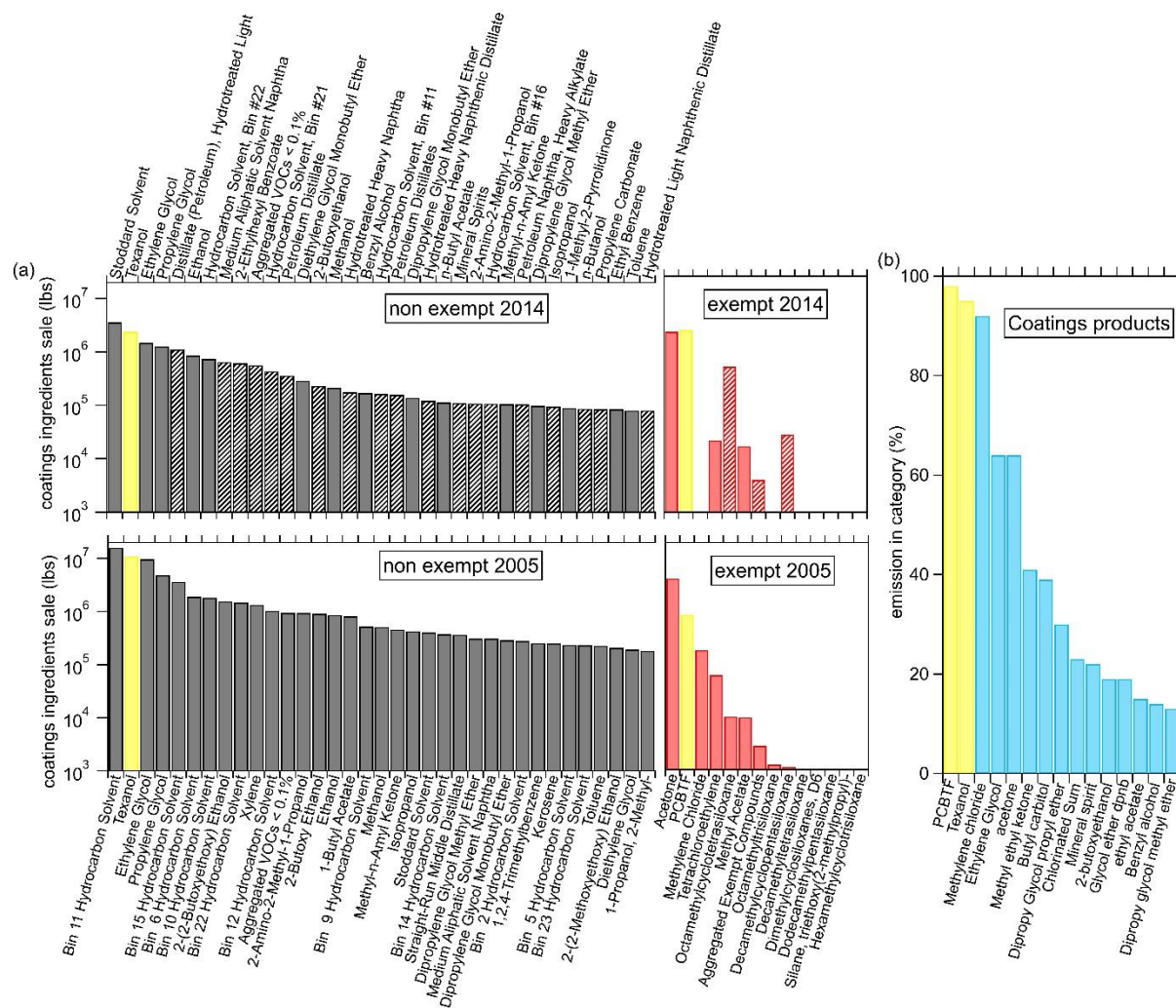
Figure 9: (a) The sale of top 35 non-exempt and the exempt VOC ingredients for coatings in 2005 and 2014 in California together with the (b) fraction of emissions in the coatings category of the 15 highest VOCs as determined by the FIVE-VCP inventory calculated using the method of McDonald et al. (2018a). The solid bars in the 2014 data indicate compounds that were detected in ambient or product testing.
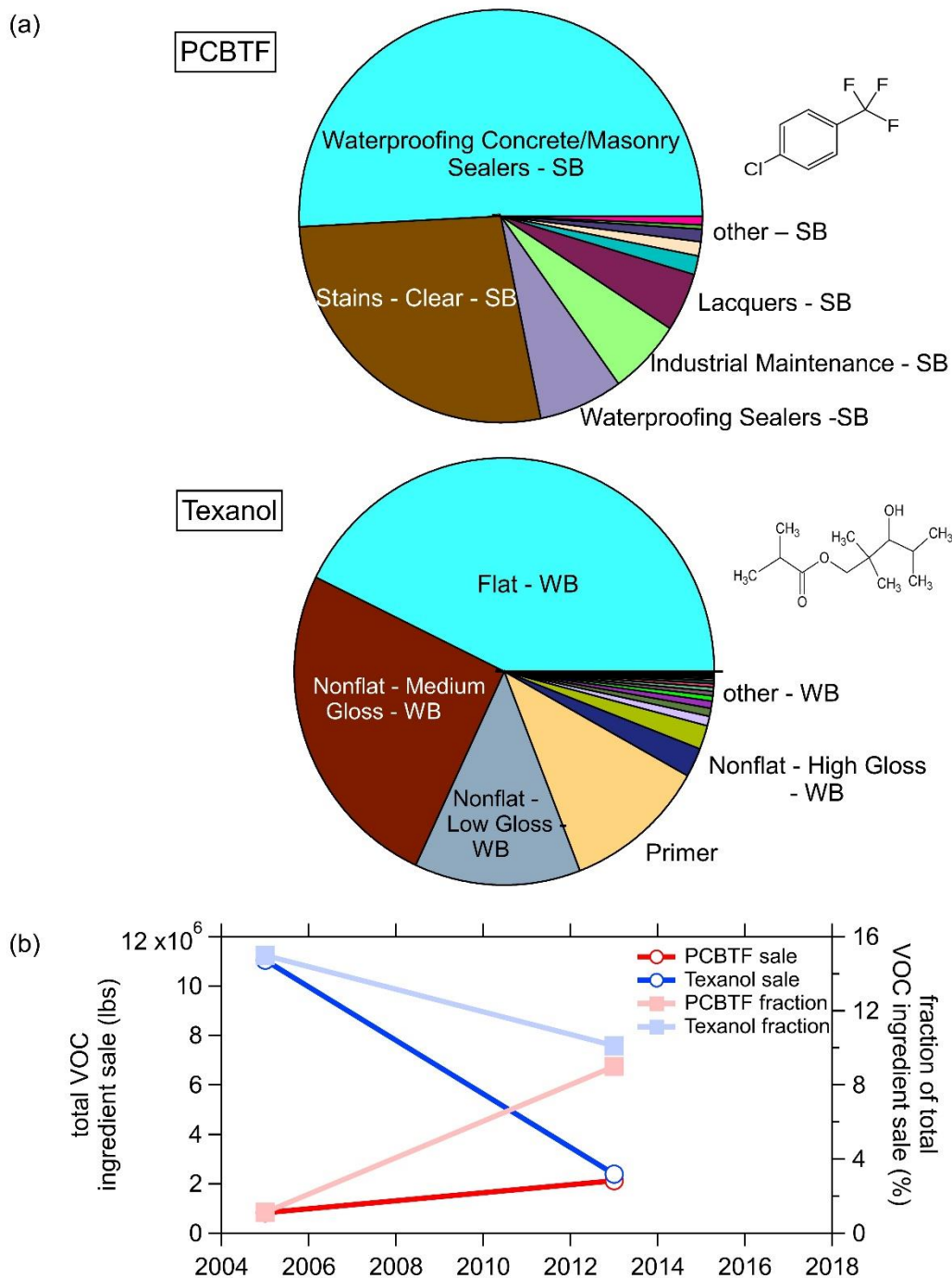
Figure 10: (a) PCBTF and Texanol use in solvent-borne (SB) and water-borne (WB) product categories in California and their (b) trends in sales and emissions.