Response to Referees

We thank all three referees for their helpful reviews and constructive commentary. The manuscript has been revised accordingly with our responses interspersed in black text.

Anonymous Referee #1

The authors present a compelling overview of Texanol and PCBTF emissions from coatings making the case for these compounds as specific tracers for water based and solvent based coatings. The authors accomplish this with an impressive synthesis of laboratory, ambient, and reported data. This paper makes a significant contribution to the study of VCPs, and I recommend it be published with minor revisions.

Mobile platform measurements show “hotspot” behavior for PCBTC, and perhaps Texanol, indicative of emission from manufacturing or construction sites. Neither compound correlates with transportation (CO) or PCP usage (Siloxane D5, population density). Taking advantage of stagnant meteorological conditions, the authors also estimate emissions for the two proposed tracer compounds.

Furthermore, using ingredient and sale data for coatings (at least in California), they show these compounds are both commonly and specifically used in coatings. This establishes a good basis for a tracer: the compound is measurable and specific to the category.

Laboratory experiments are used to qualitatively examine the headspace emissions of 19 products. I believe that this information is useful, however I have some concerns about the experimental design. Are you concerned that the water trap could systematically remove water soluble compounds? How sensitive were recoveries for water soluble compounds to the water trap temperature? I understand that this is designed to be quantitative and not qualitative, but the fact that Texanol cannot be detected by this method suggests the data in Figure 4 should be interpreted with some caution. I am fine with the presentation of what was detected, but would like to see more of a disclaimer of what may not be detected.

We agree that the sample pre-concentration and GC system was not thoroughly characterized to analyze all possible volatile and semi-volatile compounds. We specifically designed the system to capture the majority of compounds in the C3-C10 range that are typically observed in ambient air, while simultaneously maintaining a relatively short cycle time. With these objectives, the PTR-ToF-MS is able to sample in-situ for 75% of the time, while periodically taking GC samples to obtain additional information about structural isomers and to pre-concentrate samples to lower the detection limits of certain compounds.

The following text was added to section 4 (Headspace and Evaporation Measurements):

“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 following text was added to the supplement:

“Calibration standards containing components with carbon numbers ranging from acetone (C3) to monoterpenes (C10) were tested to ensure that compounds were trapped and released through the water trap, sample trap and sampling lines and could be quantitatively detected by the PTR-ToF-MS. Both polar and non-polar compounds were tested including acetone, isoprene, BTEX compounds, indene, crotonaldehyde, 2,3, methyl buten-2ol, and methyl ethyl ketone. To analyze larger (and less volatile) molecules such as C12-C15 alkenes, sesquiterpenes, tri-isopropyl benzene or Texanol (C12), the trapping system would have required modifications. Among these are higher transfer line temperatures, higher water trap temperature, longer sampling times, higher GC oven temperature and possibly a different analytical column. Since the initial characterization included identification and quantification of the vast majority of VOCs observed in ambient air with a total cycle time of approximately 15 minutes, the design criteria were met. Further efforts to analyze heavier or lighter compounds (e.g. acetylene) were not pursued."

Evaporation experiments show that among the category of "coatings", g VOC per kg product emissions can vary tremendously. It would be nice to have more than one example of a product within each subcategory (ie more than one "Latex paint"), however that may be outside the scope of this study. The authors show that the majority of VOC emissions occur shortly after application, and again the amount emitted and the time frame of emission vary within the category of coatings. The emissions presented in Figure 4 are great!

As described in Section 2 (Laboratory Measurements), the headspace of nineteen total products were tested, but only a few were sub-selected for evaporation experiments. The nineteen products varied tremendously and we focused on selecting products for the evaporation experiments that ranged in total VOC-content, but also included both water-borne and solvent-borne products that emitted frequently detected compounds, such as Texanol and PCBTF.

Before giving more specific notes, I would like encourage the authors to eventually add their PTR-ToF-MS findings to the PTR Library (Pagonis, D., Sekimoto, K. and de Gouw, J. A.: A library of proton-transfer reactions of H3O+ ions used for trace gas detection, J. Am. Soc. Mass Spectrom., 2019.) The application of GC before PTR should give rich fragmentation information for compounds that would help further research in this field.

We thank the referee for their suggestion and will continue to be in touch with Joost de Gouw to add to the PTR-library spreadsheet as additional VOCs are identified and fragmentation patterns are measured with the GC-front end.

Some specific notes to follow:

Experimental methods: please list the exact masses on which you measure Texanol and PCBTC.

Thank you for pointing out this was not included in the text. This information is included in Gkatzelis et al. (2021a), however, it should also be included in this manuscript. We have added the following text to the Experimental Methods Instrument subsection: "Texanol ($C_{12}H_{24}O_3$) was measured as a dehydrated fragment at *m/z* 199.169 ($C_{12}H_{22}O_2 \bullet H^+$) and PCBTF ($C_7H_4ClF_3$) was detected at *m/z* 160.996 ($C_7H_4ClF_2$) from the loss of fluorine."

Please list the temperature at which you conduct the laboratory experiments. One would suspect evaporation rates are highly temperature dependent. So much so that this may be worth mentioning in the discussion section as well!

We have added in the Laboratory Measurement section that the evaporation experiments were performed at room temperature. At the suggestion of Referee #3, we have added additional experimental details about the headspace analyses in the same section.

Lines 33-35: VCPs as petrochemical organics: I would like a little clarification in the writing here. VCPs are defined as: VOCs that are ingredients of, and directly emitted from, coatings, adhesives, inks, personal care products, and cleaning agents (also pesticides if you would like to add). However, this sentence may leave the reader with the impression that they are necessarily petrochemical in origin, which is not true (Just as an example, McDonald 2018a include ethanol and monoterpenes as VCPs. I don't think either of these chemicals have a significant petrochemical source.) This sentence is technically correct, as many VCPs are of petrochemical origin, but I think it is especially important that while this term is somewhat young we really hammer down its strict definition.

We thank the reviewer for highlighting this detail and agree that while VCPs is a relatively infant term, we should limit confusion where possible. We have modified the following text to emphasize these are VOC emissions from volatile chemical products, removed the mention of "photochemical organics," and added "pesticides" to the list as suggested.

Adjusted text: "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 in the urban atmosphere (McDonald et al., 2018a)."

Lines 42-43, ibid.

We believe that the emphasis of the following sentences is important as it highlights the relative importance of both personal care products and coatings and therefore prefer to keep the text as is.

L73 delete "a" : Corrected L99 "was" to "were" Corrected

Line 212: "while emissions from VCPs scale linearly with the number of people" This is contradicted by the previous evidence showing that these two VCPs do not correlate strongly with population density. Do you mean PCPs rather than VCPs?

We thank the reviewer for their attention to detail and we will emphasize that personal care products and other daily use VCPs have been shown to scale linearly with population density to avoid later confusion when Texanol and PCBTF are shown to have poor correlations with population density.

Text at L212 changed to: "while emissions from personal care products and other daily-use VCPs driven by human activity scale linearly with the number of people"

Lines 223-226 I see you are detecting Texanol on the dehydrated fragment, certainly expected for an alcohol. I would add that an isomer on this mass would be menthyl acetate, a terpenoid and flavor/odor additive. Seeing as you have calibrations of texanol, is there a fragmentation pattern that could be used to determine if there is interference in the ambient data?

Gkatzelis et al. (2021a) noted that the signal at *m/z* 199 in the winter was expected to be predominantly related to coatings, however, they did note this mass might be influenced by other compounds in the summer, especially those formed via chemical processing based on persistent high levels during midday hours and positive-matrix-factorization (PMF) results of the same dataset (Gkatzelis et al., 2021b). We have made note of these summer-time ambient interferences later in this same section (Ambient Measurements of PCBTF and Texanol).

Line 337, and figure 7a: should values these be normalized to the initial mass of the product used?

We define the emission rate here as the mass emitted per unit time. The mass concentration of each species (mg m^{-3}) was multiplied by the gas flow rate across the product through the Teflon chamber. The total mass emitted is normalized by the initial mass of the product when calculating an emission factor in units of mass emitted per mass applied (g kg^{-1}).

Figure 1b shows clearly shows PCBTF's "hotspot" behavior. Texanol, on the other hand does not show much use in the winter, which is helpful in showing that it does not follow CO or PCP patterns. However, in the summer the two largest spikes seem to align with large spikes of D5. Is this correct? If so, see my note regarding a possible interference from menthyl acetate.

The actual correlation between D5 and Texanol during the entire summer sampling period is poor (R^2~0.2). Occasionally, the enhancements are well correlated over short periods of time. This might be related to oxidation products detected at *m/z* during the summer or other possible interferences as you suggest. This is described in detail in Section 3 (Ambient Measurements). Figure 1a also emphasizes the "hotspot" behavior of Texanol as you see the largest enhancement in the northeast region of the map where population density is low.

Figure 2a: Legend is in units of people per square kilogram. Should be per square kilometer. Corrected

Figure 3: I think you could remove this figure. At the very least, remove the fits in 3a. The lines trick the eye into finding patterns that the R-squared says are not present.

We believe Figure 3 is a useful as its correlation with population is shown to be weak and can be compared to other VCP tracers in Gkatzelis et al. (2021a). Figure 2 shows that the highest mixing ratios generally occur in areas of the highest population density within a city, however, enhancements are dominated by short, spatially isolated plumes. Figure 3, ties all the sampling cities together that varied in absolute population density. Additionally, we see a strong separation between summer and winter measurements for both potential tracers.

Figure 5: Significant figures on the ppb/mg labels. 2? 3? Corrected

Figure 6: Consider using a left and right y axis rather than a VOC multiplier. I'm not certain, but it may read better.

The first graphs generated for these plots used two axes, however, we believe using the same axis with the multiplier bolded better illustrated the mass and time-dependent overlap between the two methods.

Figure 10b: this figure is confusing to read. Consider another representation. Maybe a (grouped?) bar chart.

We believe it is important to show that the relative fraction of PCBTF and Texanol use is comparable even with significant changes in total sales in recent years. We generated a figure using a grouped bar chart as suggested by the Referee and found similar issues as the data currently available remains limited. As such we believe the current Figure still effectively demonstrates that PCBTF and Texanol use is comparable even with declining Texanol sales.

Referee #2

This manuscript considers emissions of VOCs from volatile consumer products (VCPs). There is a specific focus on emissions from paints/coatings, and the use of two compounds (Texanol and PCBTF) as tracers. The manuscript is relevant to the recent interest in VCP emissions and atmospheric chemistry in the wake of declining emissions from combustion sources.

General comments: (1) The manuscript's results are broken into three main sections: (1) ambient mobile observations, (2) laboratory samples, and (3) analysis of an emissions inventory. These three sections are not connected very well, and came across more as three stand-alone chunks rather than a single cohesive narrative. The inventory section in particular seemed to be the least connected to the other two main sections.

The focus of this study is to build on the work by Gkatzelis et al. (2021a) to help unambiguously identify VOC tracer compounds linked to coatings observed in ambient measurements. In order to better tie the three sections together, we've added the following text to the introduction:

"Presented here are ambient and laboratory measurements of vapors emitted from coatings using 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"

The remaining text in the introduction emphasizes the order by which we evaluate the performance of these VOCs as coatings tracers: (1) ambient measurements, (2) laboratory measurements, and (3) inventory evaluations. Hopefully, this description in the introduction better emphasizes the need for all three sections and we believe the information is presented in the correct order.

Comments on mobile sampling: (1) Figure 1 - what is the spatial resolution of the binning? It looks like the bins are strictly based on longitude. Is that correct? Does an east-west binning introduce any biases? I imagine that there are also strong northsouth gradients in Manhattan. (2) Are the data in Figure 1 from a single drive? Or are there road segments that were sampled on more than one occasion? If there are multiple passes over a road segment (or spatial bin), how were those handled? (3) Line 183 notes isolated plumes - this suggests that emissions are episodic. If emissions are dominated by episodic events, it underscores the importance of how the mobile sampling data are binned and averaged. It's easy to imagine a case where the data end up being biased by capturing more plumes on one sampling day, or in one neighborhood, just by luck or chance. There are multiple papers that discuss spatial and temporal averaging needs for mobile sampling data (e.g., Messier et al, ES&T, 2018; E. Robinson et al, ES&T, 2019); the authors should at least acknowledge that this literature exists. If the data in Fig 1 are from a single driving pass, the authors should be clear about this, and they should also acknowledge that the data therefore represent a snapshot more than the typical or long-term spatial pattern.

We'll address the first three questions concerning mobile emissions together as there is significant overlap. The mobile laboratory measurements are shown as bars with median concentrations binned by longitude at 0.02 degrees. The median value reduces the effect of outlier observations on the comparison. Drives were conducted for several days in both the winter and summer. There are instances of repeated visits across different sampling days or within the same longitudinal bins, and in these instances the average was taken. We will add text to detail this in the manuscript. In NYC, the population density varies across its five boroughs and the largest population gradient is seen longitudinally. Ground-site measurements were used to investigate longer-term temporal patterns, while the aim of mobile sampling was to show spatial patterns. Coggon et al. (2018) and Gkatzelis et al. (2021a) have shown select volatile chemical products used on a daily-basis, such as personal care products (i.e. D5-siloxane), have strong correlations with population density. Gkatzelis et al. (2021a) shows these strong correlations for other VCP tracers such as monoterpenes (fragrances) and D4-siloxane (adhesives). The aim of this section is to show that the correlation with population density is not as strong for PCBTF and Texanol. As the Referee mentioned the emissions for these two compounds were driven by episodic events and this conclusion is supported by its poor correlation with population density while other VCPs continue to show a strong dependence in several cities. We make it clear in the manuscript that these are "short, spatially isolated plumes" and the ground-site measurements represent more-long term temporal patterns. We add a sentence to clarify the intention of the mobile measurements as the aim was not to identify long-term spatial patterns.

Added details of sampling strategy: "Multiple drives across the two seasons were conducted and longitudinally overlapping drives were averaged."

"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."

Added to the references: Messier, K. P., Chambliss, S. E., Gani, S., Alvarez, R., Brauer M., Choi, J. J., Hamburg, S. P., Kerckhoffs, J., LaFranchi, B., Lunden, M. M., Marshall, J. D., Portier, C. J., Roy, A., Szpiro, A. A., Vermeulen, R. C. H., Apte, J. S.: Mapping air pollution with Google Street View cars: Efficient approaches with mobile monitoring and land use regression, Environ. Sci. &Technol., 52, 12563−12572, doi: 10.1021/acs.est.8b03395, 2018.

Added to the references: Robinson, E. S., Shah, R. U., Messier, K., Gu, P., Li, H. Z., Apte, J. S., Robinson, A. L., Presto, A. A.: Land-Use regression modeling of source-resolved fine particulate matter components from mobile sampling, Environ. Sci. & Technol., 53, 8925−8937, doi:10.1021/acs.est.9b01897, 2019.

(4) The correlations of PCBTF and Texanol with CO (Fig 1) are useful context. However, I would also like to see the correlation between PCBTF and Texanol. A visual inspection of the top part of Fig 1 suggests that these are not correlated very well. Given that the source(s) are the same, is this poor correlation expected? (It seems that this poor correlation is discussed in more detail in the section on the laboratory experiments. Nonetheless, it would be helpful to readers to give it some attention here.)

Your visual inspection is correct, the correlation between PCBTF and Texanol is not strong during the summer season (R^2<0.1). This poor correlation is not unexpected since these compounds are emitted by different types of coatings (e.g., water-borne or solvent-borne) and are often used for different applications. We add the following sentence to this section to make this clear.

Added text: “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).”

(5) Can the authors be more specific about what they mean by "industrial" uses of paints and coatings? It seems like construction is one example of industrial use, but I can also imagine that industrial uses would include painting or coating of manufactured products. I think that these different types of industrial uses could be apparent in the data. E.g., are some of the Texanol spikes near large construction projects? In Figure 2 there seems to be a large area in northern Indiana with high PCBTF concentrations. Could this be emissions from non-construction industrial uses? My impression is that this region still has a lot of heavy industry.

We thank the reviewer for pointing out the confusion, as we must be clearer in our separation of architectural and industrial coatings as they are regulated separately. The definition of architectural coatings are products that are applied to stationary structures and their accessories. They include house paints, stains, industrial maintenance coatings, traffic coatings, and many other products. Industrial maintenance coatings formulated for their chemical and corrosion resistance are a subcategory of architectural coatings when applied to stationary structures. Generally, coatings applied in shop applications or to non-stationary structures are not considered architectural coatings and instead are categorized as industrial coatings. The formulations of many architectural and industrial coatings can be similar, therefore, when using Texanol or PCBTF as tracers, we cannot distinguish between the sources of architectural or industrial coatings. We’ve added the following text to the introduction to emphasize the distinction between these two categories:

“Architectural coatings are defined as products applied to stationary structures and their accessories, whereas coatings applied in shop applications or to non-stationary structures are categorized as industrial coatings. Both coating types can be utilized in industrial applications (e.g., construction or manufacturing activities).”

In the manuscript a lot of the confusion lies in that we had generalized the term “industrial” to include the activities of applying coatings to stationary objects. As an example, we included the industry of construction into the phrase “industrial usage patterns.” You are correct that there could be non-construction industrial uses in the manufacturing sector. To clarify we’ve changed the text to state: “emissions from coatings are influenced by industrial usage patterns, such as construction or manufacturing activity” and have eliminated the use of “industrial” in other areas of the manuscript to limit confusion.

With regards to your suggestion that different types of industrial uses could be apparent in the data, manufacturing processes generally occur indoors, often with VOC capturing systems. The indoor/outdoor exchange can still impact urban air, though it is likely strong enhancements would be only observed at or near manufacturing sites. The enhancements in PCBTF in the area of northern Indiana and in other areas of the U.S. were qualitatively observed near construction sites or near asphalting road activities. It would be a useful goal for future studies to detail enhancements near manufacturing sites, though this is outside the scope of this current manuscript.

(6) Figure 3 - Please define how the enhancement is determined (i.e., what is the background?).

We report enhancement ratios relative to benzene. Enhancement ratios are calculated using median concentrations, which reduces the impact of local emissions on calculated ratios (that would also impact the slope of a scatter plot). We subtract the background median using measurements upwind of the cities that exhibited the lowest mixing ratios from the median using measurements from regions where the population density was the highest.

We've added the following text to the Figure 3 description:

"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."

Comments on laboratory tests: (1) Figure 4 and related discussion - PCBTF is only present in the solvent-borne paints, and not in the water-borne samples. However, prior to this point, the authors assert that PCBTF is a general paint/coating tracer. I think this needs to be clarified in the previous section.

Based on the Referee's earlier comments we've added to the ambient measurement section a discussion of the correlation between PCBTF and Texanol and how the poor correlation is not unexpected because the primary sources vary depending on whether it is a solvent- or water-borne formulation. Additionally, we now modify the last sentence of the introduction to state: "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." This now alludes to a separation between water- and solvent-borne tracers at several locations in the manuscript before the laboratory measurement section starts.

(2) I do not see Texanol in Fig 4. Since that is the other tracer used in this work, I think it would be good to show it in this figure.

We detail in Section 4 that 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. Based on suggestions by Referee #1 we've added additional text in the main manuscript and supplement detailing the characterization of the GC-system.

(3) One concern that I have about VCPs is that there can be so many sources of variability - e.g., between types of coatings (e.g., indoor vs outdoor, latex vs low VOC vs oil based), between specific formulations (e.g., different gloss levels of latex paint sold by the same manufacturer), and between manufacturers. Obviously it is impossible to capture all of these sources of variability in one paper, but they should at least be acknowledged. While the paint samples used here might be representative in the sense that they can be purchased commercially, there is a lot of potential variability that is not controlled for here.

We agree that coatings formulas vary considerably and we try to illustrate this by listing all the types of coatings in the introduction and also highlighted we only sampled commercially available products and industrial maintenance coatings formulated to withstand harsher environmental conditions were not included. In order to acknowledge the limitations of this study, we add the following disclaimer into the Experimental Methods section:

Added text: “The variability in product formulation and usage is significant and the coatings in this study were selected based on availability, total VOC content, and similarity between other products tested, therefore the results do not fully capture the emissions variability of all coatings”

(4) Figure 5 - are the total emission rates indicated in the figure (e.g., 586 ppb/mg for the zero VOC paint) the average over the whole experiment, or from a portion of the experiment?

Line 275 mentions the sums of all the measured PTR-TOF signals in the “early” mass scan is identified by the labels. In order to make this clearer, we also add to the figure caption “taken from the early mass scan”

(5) Figure 7b - does this show the instantaneous or integrated emissions? E.g., the purple line for acetone flattens out around 2% very quickly. Does this reflect that the volatile components are emitted quickly (including a big burst of acetone), or does acetone keep getting emitted at around 2% of total VOCs for the entire 19 hours of the experiment?

Figure 7b shows the relative contribution of individual species to the total integrated mass over time. Therefore, the largest mass of acetone is emitted early and its relative contribution to the total mass emitted gradually levels off. After a few hours the species contributing to total VOC mass is largely driven by only a few compounds (e.g. ethylene glycol). To make this clearer the following text was added to the figure caption.

“(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.”

(6) Line 372-379 note that the trend in VOC emissions tracks the stated VOC content of the products. While that is true, there does not seem to be a linear relationship between stated VOC content and measured emissions. Latex paint emits 20x more VOCs than primer/sealer even though there is 2.5x the VOC content. There is a similarly large jump in VOC emissions between the stain and the latex paint for another factor of ∼2 change in VOC content.

We thank the referee for their attention to detail and agree that the percent emitted and content reported in g VOC/L cannot be compared directly as the density of each product would need to be considered and known to calculate a mass emitted that is directly comparable. The goal was to emphasize the qualitative agreement between the manufacturer’s content label and we have modified the wording to this effect.

Added text: “The actual density of each product would need to be known to calculate the VOC mass emitted from the content labels, thus the comparisons described above are qualitative.”

Comments on inventory section: (1) As I note above, I do not feel like this section is connected very well to the rest of the manuscript. (2) This section focuses heavily on the emissions for California. How representative is CA of the rest of the US?

We believe that the added detail in the introduction described above will better connect this section with the rest of the manuscript. We’ve shown the motivation of this work is to help unambiguously identify VOC tracer compounds linked to coatings. We do this through ambient and laboratory measurements, while the third section shows that Texanol and PCBTF are VOCs unique to the coatings category and their emissions are prevalent in inventories.

The reason this section focuses on California is based solely on the availability of data. California is the only state that conducts comprehensive surveys of coatings as detailed in the text. It is likely the product sales and usage in California are similar throughout North America. The FIVE-VCP inventory that includes data from these surveys has shown good agreement with ambient measurements in LA and NYC (McDonald et al., 2018; Coggon et al., 2021).

Referee #3

VCPs' emissions have become a very important consideration in tropospheric chemistry studies, especially those focused on developed megacity environments. It is now essential to determine the major contributors to these emissions and specific tracer species that could assist in their isolation and quantification. From this perspective, this paper certainly would be useful for the scientific community. The authors have specifically focused on emissions from coatings-related products and have approached the source from multiple investigative dimensions including laboratory investigations, ambient measurements and exploration of existing chemical speciation surveys and databases. The work is comprehensive in nature and attempts to encompass all manners of arguments to support the paper's objectives. Nevertheless, I have some concerns that need to be resolved before I could recommend the work for publication. They are listed below:

1. The introduction mostly focuses on VOCs which for the large part is fair for coatings related products. Still, to present the complete picture, I believe some acknowledgement is warranted for small IVOCs (n-alkane equivalent volatility< C14) that may be present in solvents-based coating products. The authors do lend a quick word to LVPVOCs that are currently exempt, but others have shown that LVP-VOCs are important for air quality and yet maybe underestimated due to instrumentation limitations and long emission timescales e.g. Khare and Gentner, 2018 ACP.

We agree that we should mention I/SVOCs in the same context that we describe LVP-VOCs even though our instrumentation primarily measures VOCs and only a few IVOCs. We add text to the introduction to highlight the importance of these understudied SOA precursors and their exclusion from inventories and regulations.

"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)."

Added to references: "Khare, P. and Gentner, D. R.: Considering the future of anthropogenic gas-phase organic compound emissions and the increasing influence of non-combustion sources on urban air quality, Atmos. Chem. Phys., 18, 5391–5413, https://doi.org/10.5194/acp-18-5391-2018, 2018."

2. The experimental methods section could be better knitted. For example, as a reader, I'm confused about why I am reading 2.1.1 and 2.1.2 separately. As I understand it, 2.1.2 involves coupling a GC with PTR-ToF ahead of its inlet for improved separation that also permits detection of isomers. This could be easily merged with 2.1.1 and narrated cohesively.

The experimental section is broken down into four parts: (1) description of the instrumentation (2) description of the laboratory measurements (3) description of ambient measurements and (4) description of the FIVE-VCP inventory. Based on this and later suggestions we have reorganize the experimental methods section to mirror the discussion (i.e., ambient measurements, FIVE-VCP inventory used with the ambient measurements, then laboratory measurements) and combine 2.1.1 and 2.1.2 together as suggested.

3. Similarly, in laboratory measurements subsection (in methods), I would like to see some description (with perhaps a schematic in the SI) of the headspace sampling setup in the main text. Future experimental studies on VCPs could certainly benefit from it. The current description of laboratory methods left me with questions: Was the sample well-mixed (or re-mixed) within the container before headspace sampling occurred? Was the sample transferred to a new container for headspace sampling or

was it done in the original product container? If the sample was transferred to a new container, was it collected from the core of the original product or scooped from the surface since the core may have more volatile content? What temperature was the product subjected to during emissions? How much time was allowed for air-sample equilibrium to be attained in the headspace? I understand that this was a qualitative investigation but the finer details are important to ascertain that the sample was not already partially depleted of certain volatile constituents before sampling was conducted.

We thank the reviewer for their suggestion to give greater detail on the headspace experiments and we hope the added detail will benefit future experimentalists. We add text to the main manuscript describing the sampling approach, although we believe the detailed description provides enough context that it can readily be simulated in future studies without the addition of a schematic. As a brief description, the products were mixed thoroughly and an aliquot was transferred to a new container. The container was opened to the atmosphere at room temperature and GC samples were collected every 20 minutes, resealing the container between runs. As you mentioned, these were qualitative experiments, however, the products were not allowed to dry and repeat GC runs revealed repeated peaks.

Added text: “Each product was mixed thoroughly in its original container and an aliquot was transferred into a glass vial. The headspace VOCs were sampled by placing the product container that was open to the atmosphere within a few centimeters of the PTR-ToF inlet. The instrument inlet tubing was a short piece of PFA Teflon to limit inlet losses or delays (Deming et al., 2019). The container was closed between GC sample intervals (20 min) and zero air was sampled between runs.”

Added to references: “Deming, B. L., Pagonis, D., Liu, X., Day, D. A., Talukdar, R., Krechmer, J. E., de Gouw, J. A., Jimenez, J. L., and Ziemann, P. J.: Measurements of delays of gas-phase compounds in a wide variety of tubing materials due to gas–wall interactions, Atmos. Meas. Tech., 12, 3453–3461, https://doi.org/10.5194/amt-12-3453-2019, 2019.”

4. Lines 131-132: Please define extreme environmental conditions. Non-combustion emissions such as those from coatings would be temperature-dependent. Could excluding products used in high-temperature environments affect/bias your results in any way, especially the emission rates?

Industrial maintenance coatings are defined as high performance architectural coatings applied to substrates formulated for extreme environmental conditions such as: (a) Immersion in water, wastewater, or chemical solutions or chronic exposure of interior surfaces to moisture condensation; (b) Acute or chronic exposure to corrosive, caustic, or acidic agents, or similar chemicals, chemical fumes, chemical mixtures, or solutions; (c) repeated exposure to temperatures above 121 C; (d) Frequent heavy abrasion, including mechanical wear and frequent scrubbing with industrial solvents, cleansers, or scouring agents; (e) Exterior exposure of metal structures. The focus of this study was on readily-available coatings products and most commercially available products are formulated to withstand some degree of environmental exposure. There is significant variability in coatings products, and only a subset of products was selected for this analysis and we do not recommend the emission rates calculated are representative of all coatings. Each individual product, whether it be formulated for extreme or normal conditions, has its unique composition and the aim of this study was to identify compounds prevalent across several products supporting their use as tracers and to evaluate emissions after initial application at room temperature conditions. It is certainly possible the formulations for the products designed for extreme conditions might not include PCBTF and Texanol and some products likely don’t include these compounds as ingredients. At the suggestion of Referee #2 we’ve added text to the Laboratory Measurement section noting product variability with a disclaimer that these products were selected based on availability, VOC content, and chemical similarity to other tested products.

5. Lines 132-133: It is unclear how this was positioned. Was the PTR-ToF inlet exposed to an open product container? What was the distance between the inlet and the product? Was the direction of the airflow between the inlet and sample controlled? The issues go with point 3 above.

We've addressed these questions by expanding on the description of the headspace experiments in the experimental section as suggested in point 3 above.

6. Lines 138-140,309: Please mention what was the range of the emissions velocity from the product's surface into the air flow. For quantification purposes, it is important that the emissions velocity is representative of environmental conditions in which the product is to be used. Otherwise, please provide an explanation for how the measured emission rates could be justified as relevant in real-world conditions, and also from a modeling perspective. What temperature was each sample subjected to during the chamber experiments?

As requested earlier, we have added to the experimental details that the evaporation experiments were all conducted at room temperature. An emissions velocity from the product's surface was not measured, instead a constant flow of synthetic zero air continuously passed through the Teflon coated chamber as noted in the Laboratory Measurements section. Only a subset of products was selected for this analysis and we do not recommend the emission rates calculated are representative of all coatings. The emission rates qualitatively highlight the differences between product types with varying VOC content and demonstrate the time-dependent variability following application.

7. It would probably help to keep the discussion sections consistent with the experimental subsections or vice versa. As a reader, I wasn't sure why I landed on a discussion section specifically focused on Texanol and PCBTF right after the methods. It might be better to present the bigger picture, broader details about the chemical speciation of tested products and field measurements, before narrowing it down to the proposed tracer compounds.

We note that the order of the Experimental Methods did not mirror the discussion text and we have now reordered the methods section to give a better flow between the two sections. Additionally, based on the suggestion of Referee #2 we added text to the introduction that highlights the reasoning for the order of the manuscript since the focus of this study is to help unambiguously identify VOC tracer compounds linked to coatings observed in ambient measurements. This rationalizes the structure of the manuscript starting with initial ambient observations of two potential tracers, followed by confirming their prevalence in several coating products, and finally evaluating their uniqueness and usage in inventories.

8. Section 4 "Headspace and Evaporation Measurements" could be written better. The paragraphs read disjointed and I had to scroll up and down repeatedly to properly understand the content. For example, line 244 marks initiation of the discussion of headspace sampling which in line 268 suddenly shifts to evaporation experiments without any ramp.

To make the section read clearer we've added a sentence to show a separation between the discussion of headspace analyses and evaporation experiments. The headspace discussion already begins with the following sentence: "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 smoothly transition to the discussion focused on evaporation experiments, the introduction to the paragraph at L268 is reordered and modified as follows: "During evaporation experiments, the products were introduced into an enclosed chamber and sampled over longer periods to investigate changes in evaporative emissions." The subsequent paragraphs describe results from the evaporation experiments, however, there is still considerable overlap between the headspace and evaporation experiments when discussing the dominant emissions from each product. The main text explicitly references GC-chromatograms or the GC analysis when detailing those results.

9. Lines 186-187: If PCBTF and Texanol are predominantly from construction activities, some explanation is required for why their mixing ratios were dominated by short, isolated plumes? I would expect construction activity in an area to be decaying but continuous source of the tracer, especially if the source is industrial coatings. Or is this because the mobile lab was in continuous movement and saw a temporary spike when it happened to be passing by a source? I think it is the latter based on the opening statements in the conclusion paragraph. However, it is important to clarify this, or else source behavior could be easily misunderstood.

It is likely the confusion results from the first sentence of the Ambient Measurements of PCBTF and Texanol. We will remove “ground site” from the first sentence as the initial discussion focuses on mobile measurements and ground site measurements aren’t considered until temporal trends are discussed. This should alleviate the confusion.

10. Lines 349-351: The authors mention that acetone and formaldehyde did not emit as expected based on thermodynamic considerations but leave it at that calling it “complicated”. I found the trends in Figure 7b very interesting and would very much like to see some explanation, even if just reasonable speculation from the authors for these observed trends.

It is very likely fragmentation plays an important role here, with significant fragmentation to both these masses this complicates using saturation vapor concentrations to predict peak emission. There are also other variables likely in play as described in the text (e.g., composition, drying time, substrate interaction/properties, etc.)

Added text: “Fragmentation of larger compounds with a range of volatilities, including glycols, to the *m/z* of acetone and formaldehyde is one possible explanation for these discrepancies”

11. Figure 2b could go into the SI. Since these are mobile measurements, the concentration measured is not singularly dependent on time of day but also the location of the vehicle. Hence, the figure is confusing and not substantial enough in my perspective to warrant a spot in the main text. Would the highest peaks still be observed between 2-3 PM if the vehicle was at some other location? The figure caption should clearly mention that these are mobile laboratory-based ambient measurements.

Figure 2b was initially included to further emphasize that PCBTF shows hot spot, episodic behavior. However, we agree with the Referee that the figure does not add significantly to the manuscript and Fig. 2a clearly shows mobile measurements of spatially, isolated plumes. We have removed Figure 2b.

Minor points: -Line 244-245: Nitpicking here but measuring the headspace by PTR-ToF is unclear. Sampled vapors from the headspace is more accurate. Corrected

-Fig. vs. Figure is used inconsistently in the text.Line 268-“Figure 5a”, line 277-“Fig. 5b”. Similarly for 6. Line 310 says “Figure 6”, line 314- “Fig. 6”. Please check others.

The manuscript preparation guidelines outlined by the manuscripts state: “The abbreviation "Fig." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence, e.g.: "The results are depicted in Fig. 5. Figure 9 reveals that...".

-Line 392: increased “from”. Corrected

-Figure 3: (a) has illegible overlap in the figure. –

There is very limited overlap for the labeled points. We have eliminated the second Chicago from the top of panel (a) to eliminate the most significant overlap

Figure 5: is clumsy. Compound identifications overlap and are not readable in several places. Consider using arrows where necessary. Some compound names are not fully printed in the spectra. -All across the figures, the legends sometimes start with block letters and other times with small letters. Please correct the inconsistency.

We have limited the number of species labeled in the figure and started each species name with capital letters to clean up the image. The main text is now changed from "The major peaks in each product are labeled" to "Select major peaks in each product are labeled"

Voluntary Changes: We have updated the reference of Gkatzelis et al. (2020a) to Gkatzelis et al. (2021a) as it is now published. We have also updated to the current year (2021) for manuscripts currently submitted for publication (i.e., Coggon et al. 2020 and Gkatzelis et al. 2020b)

Gkatzelis, G. I, Coggon, M. M., McDonald, B. C., Peischl, J., Aiken, K. C., Gilman, J. B., Trainer, M., and Warneke, C.: Identifying volatile chemical product tracer compounds in U.S. cities, Environ. Sci. Technol., submitted, 55 (1), 188-199, doi: 10.1021/acs.est.0c0546, 2021a.

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 fuel VOCs in Los Angeles and other cities in the United States (McDonald et al., 2018a; Coggon et al., ~~2020~~2021). Reductions in tailpipe emissions of VOCs from gasoline vehicles are slowing, and diminishing returns from emission control technologies have been reported for on-road vehicles (Bishop and Haugen, 2018). With slowing trends in ozone precursors and shifts in ozone production regimes, decreases in ozone design values may have slowed as well (Parrish et al., 2017).

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

The composition and emissions of chemical products have changed significantly in recent decades in an effort to reduce the ozone (O_3) and secondary organic aerosol (SOA) formation potential (Weschler, 2009; CARB, 2015; Shin et al., 2016). For example, water-borne paints are increasingly replacing solvent-borne paints, while simultaneously many VOC ingredients are being replaced with water (Matheson, 2002), “exempt” VOCs, or low-vapor-pressure VOCs (LVP-VOCs) (Li et al., 2018). The California Air Resources Board (CARB) defines "exempt” VOCs as compounds that are not expected to meaningfully contribute to ozone formation due to their low reactivity in the atmosphere. Examples include acetone, ethane, perchloroethylene, methyl acetate, and parachlorobenzotrifluoride (PCBTF). CARB also exempts several LVP-VOC, which are defined as chemical compounds containing at least one carbon atom and a vapor pressure less than 0.1 mm Hg at 20°C, organic compounds with more than 12 carbon atoms, compounds with boiling points greater than 216°C, chemical mixtures comprised solely of compounds with more than 12 carbon atoms, or as the weight percent of a chemical mixture that boils above 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 gravimetricallyprepared 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. ~~2020a~~2021a). Texanol ($C_{12}H_{24}O_3$) was measured as a dehydrated fragment at *m/z* 199.169 ($C_{12}H_{22}O_2 \bullet H^+$) and PCBTF ($C_7H_4ClF_3$) was detected at *m/z* 160.996 ($C_7H_4ClF_2$) from the loss of fluorine. The sensitivity of compounds that were not calibrated were calculated according to Sekimoto et al. (2017).

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

~~2.1.2 GC Front End to PTR-ToF-MS~~

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

The GC consists of a 30 m DB-624 column (Agilent Technologies, 30 m, 0.25 mm ID, 1.4 µm film thickness) and oven combination identical to the system described by Lerner et al. (2017), a liquid nitrogen cryotrap, and a 2 position 10-port valve (VICI) to direct gas flows. The column was selected to measure polar and nonpolar VOCs in the approximate range of ~~C4~~C3-C10. The effluent of the GC column is injected into the PTR-ToF inlet. Depending on the application, 1-5 minute samples can be collected and chromatogram lengths of 10-20 minutes can be chosen such that the total ~~run~~ trapping and analysis time is between 15 and 30 minutes. LabVIEW (National Instruments) software controls the sequence of events, hot and cold trap temperatures, valve switching, sample flow and carrier gas flow. The detection limit for commonly detected VOCs (e.g., isoprene, benzene, xylenes) using this cryofocusing system is ~ 5 pptv.

~~2.2. Laboratory Measurements~~

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

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

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

The field measurements used to evaluate ambient measurements of coatings are described in detail by Coggon et al. (~~2020~~2021) and Gkatzelis et al. (~~2020a~~2021a). Briefly, measurements were conducted during the New York Investigation of Consumer Emissions (NY-ICE) campaign in winter (March 5 – 28, 2018) and the Long Island Sound Tropospheric Ozone Study (LISTOS) in summer (July 5 – 24, 2018) to characterize the emission profile, strength, and seasonality of VOCs emitted from VCPs.

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

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

The Fuel-based Inventory of Vehicle Emissions and Volatile Chemical Products (FIVE-VCP) emission inventory used in this work was described in detail by Coggon et al. (~~2020~~2021). Briefly, VCP emissions were estimated from chemical production data determined from a “bottom up” mass balance of the petrochemical industry. The VOC speciation profiles were updated for the coatings category to include more recent architectural coating surveys by the California Air Resources Board (CARB) (CARB, 2018). The per capita use of VCPs specific to the coating sector was estimated and combined with VOC emission factors (in g VOC per kg product) reported by McDonald et al. (2018a) that is based on a review of indoor air quality literature. The VCP emissions were spatially apportioned using US Census block population data (Bureau USC, 2020a) and the temporal patterns are taken from the National Emissions Inventory (NEI) 2014 (EPA, 2017).

Mobile source emissions are estimated utilizing a fuel-based approach based on fuel sale reports for on-road and off-road engines. CO and VOC emission factors (in g VOC per kg fuel) were taken from the compilation by McDonald et al. (2018a) and updated to 2018 by Coggon et al. (~~2020~~2021). The emission factors include tailpipe emissions from running exhaust, enhanced emissions associated with cold-starting engines, and evaporative gasoline VOC sources. The spatial and temporal emission patterns of mobile source engines are taken from the NEI 2014 (EPA, 2017).

2.4. Laboratory Measurements

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

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

3 Ambient Measurements of PCBTF and Texanol

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

The “zero VOC”, low odor paint and the primer/sealer paint have relatively low emissions, which were dominated by small oxygenated VOCs (methanol, ethanol, formaldehyde, and acetone). The primer/sealer paint also emitted Texanol, which can be expected from the ingredients of many water-borne products. The Texanol signal measured in the laboratory experiments has no contribution from the oxidation products that were identified as potential interferences during ambient summer sampling (Gkatzelis et al., 202~~0~~1a; Gkatzelis et al., ~~2020b~~2021b). Methanol, ethanol, and acetone emissions are expected ingredients, as listed in the FIVE-VCP inventory. Formaldehyde is not an ingredient, but emissions might be expected from the use of preservatives that include formaldehyde-condensate compounds that rely on the release of free formaldehyde from the hydrolysis of a parent structure such as dimethylol glycol and dimethylol urea. Dimethylol glycol and dimethylol urea are routinely used as biocides in water-borne paints and fungicidal products, but have now been widely replaced by other compounds such as isothiazolinones (Salthammer et al., 2010). Ethylene glycol is an abundant ingredient in architectural coatings sales surveys (CARB, 2018), and has been observed in an indoor air study during a painting event (Pagonis et al., 2019). The signal at mass 45 ($C_2H_4O{\bullet}H^+$) is typically attributed in PTR-MS studies to acetaldehyde (de Gouw and Warneke, 2007), but ethylene glycol fragments mostly to *m/z* 45. Acetaldehyde was present in the GC experiments and although ethylene glycol was not observed, as it is likely lost in the water trap, its dominance in architectural coatings and paints suggests it may be a dominant species at that mass.

The total VOC signal was significantly larger by an order of magnitude for water-borne latex paint than for the two other water-borne paint products, with ethanol being the biggest emission. In addition to the small oxygenated VOCs, larger compounds such as dipropylene glycol monobutylether and other ketones and acetates were emitted.

Several species listed as ingredients in CARB coatings surveys were tentatively identified in the paint emissions as ethylene glycol, methyl-n-amyl ketone, 1-methyl-2-pyrrolidinone, and methyl-, vinyl-, ethyl-, and butyl acetate. For butyl acetate, the major peak in the GC chromatogram at mass 117 correlated strongly with peaks at *m/z* 61 and 43, which are known fragments of the parent ion (Buhr et al., 2002).

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

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

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

For the solvent-borne polyurethane coating in Fig. 6d, the mass emitted as VOCs exhibited a temporal profile that more closely mirrored the mass lost recorded by the scale. The similarity in the emission profile and weight loss indicate that the majority of the weight loss from the solvent-borne stain is due to VOC emissions with only a small fraction of weight loss from other undetected compounds or underestimation due to poor sensitivity to hydrocarbons. The mass remaining on the scale indicated that about 40% of the weight remained as solids or unevaporated VOCs, which is within 5% of what is expected from the manufacturer reported VOC content of 550 g L^{-1}. Figures 6b and 6d represent two extremes and it is likely each product will have different evaporative properties depending on the overall composition and atmospheric conditions. Figure 6 also shows that for the (a) "zero VOC" paint and (d) polyurethane stain, the VOCs emitted in the first hour account for over 50% of the total mass emitted as measured VOCs over the course of this experiment. Latex paint (c) takes an additional hour and the primer/sealer (b) takes nearly 6 hours for the majority of the measured VOCs to evaporate. The experiment did not complete to dryness, thus the total mass measured is likely an underestimate, and potentially under-account semi- and intermediate-volatility VOCs that have a lower volatility. Continued emissions from dry-paint have been observed following complete water evaporation (Clausen, et al., 1991; Hodgson et al., 2000), though emissions from the dry-film were not investigated here.

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

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

The PTR-ToF also detects several inorganic species such as ammonia, though the signal at *m/z* 18 suffers from high background signal and has only been quantified for large emission sources such as biomass burning (Karl et al., 2007; Müller et al., 2014; Koss et al., 2018). There was a clear enhancement of ammonia in all water-borne coatings that was absent in the solvent-borne coatings, and it is likely mass emitted as ammonia can be important in water-borne products as it is commonly used as a pH stabilizer. The ammonia PTR-ToF sensitivity derived from a comparison with an FTIR during biomass burning sampling (Koss et al., 2018) was used to estimate the mass emitted as ammonia for the latex paint. The total mass emitted as ammonia (2.1 mg) rivaled the VOC mass (2.3 mg), and shows ammonia emissions can be significant from certain water-borne products. There was no direct calibration of ammonia during these experiments and therefore the discussion focuses on VOCs only.

Table 1 summarizes the results of the evaporation experiments. As expected, the solvent-borne polyurethane VOC emissions accounted for the greatest amount of total mass detected (83%), which is likely a lower limit estimate since the PTR-ToF is less sensitive to hydrocarbons. The trend in the VOC emissions qualitatively tracks the VOC content reported on the product labels (g L^{-1}). The "zero VOC" paint data sheet reported < 5 g L^{-1} VOCs and emitted 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, 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 VOC content of < 550 g L^{-1}. We note that the emission factors are underestimated since the experiments did not complete to dryness. The actual density of each product would need to be known to calculate the VOC mass emitted from the content labels, thus the comparisons described above are qualitative. The VOC emission rates for each product, averaged during the 19-hour experiments, also mirror the VOC content. ~~We note that the emission factors are underestimated since the experiments did not complete to dryness.~~

5 CARB Architectural Coatings Survey Data

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

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

The South Coast Air Quality Management District (SCAQMD) also reports data from coatings sales and emissions from 2008 to 2017 (reproduced in Fig. 8b). These data are part of the CARB survey and represent half of the California-wide emissions. The sales in SCAQMD have been relatively steady ranging from 35-42 million gallons with only slight increases since 2009, while the emissions have decreased significantly from 2008 to 2014 and were constant around 11 tons/day from 2014 until 2017. This data set extends the CARB surveys and might indicate that the overall emissions have not continued the steep decease after 2014, so that 2014 CARB data might still be representative of the 2018 ambient measurements presented above.

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

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

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

More details of the use of PCBTF and Texanol are shown in Fig. 10, where panel (b) shows that the use of Texanol has strongly declined, while the use of PCBTF has increased such that they had comparable ingredients sales in 2014. Both were around 10% of the total sale each. The pie charts in Fig. 10a show that PCBTF is mainly used as a solvent in solvent-borne products, such as sealers, stains and polyurethane finishers. Texanol is used in water-borne products as a coalescent for latex and other paints (Lin and Corsi, 2007). In summary, the CARB survey results in Fig. 8, 9, and 10 indicate that PCBTF might be a good atmospheric tracer for solvent-borne coatings and Texanol for water-borne coatings, even though the use of Texanol is rapidly declining.

6 Conclusion

Mobile field measurements in urban areas show that compounds largely associated with architectural coatings, such as PCBTF and Texanol, were observed from point source locations near and around construction activity. Unlike other VCP emissions previously described by Gkatzelis et al. (~~2020a~~2021a), these molecules do not correlate strongly with population density, which suggests that their emissions are not driven by wide-spread, individual usage. In contrast, the spatial and temporal patterns suggest that coating emissions are from discrete ~~industrial~~ applications, such as architectural and construction projects.

Headspace analysis measured with a PTR-ToF and GC front end confirmed the identity of many VOCs cataloged as ingredients in inventories compiled by CARB from architectural coating surveys. The “zero VOC” paint analyzed had low VOC emissions dominated by small oxygenates including methanol, ethanol, and acetone, with negligible emissions from smaller hydrocarbons and aromatics. The solvent-borne polyurethane stain emissions were 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.

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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.

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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

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

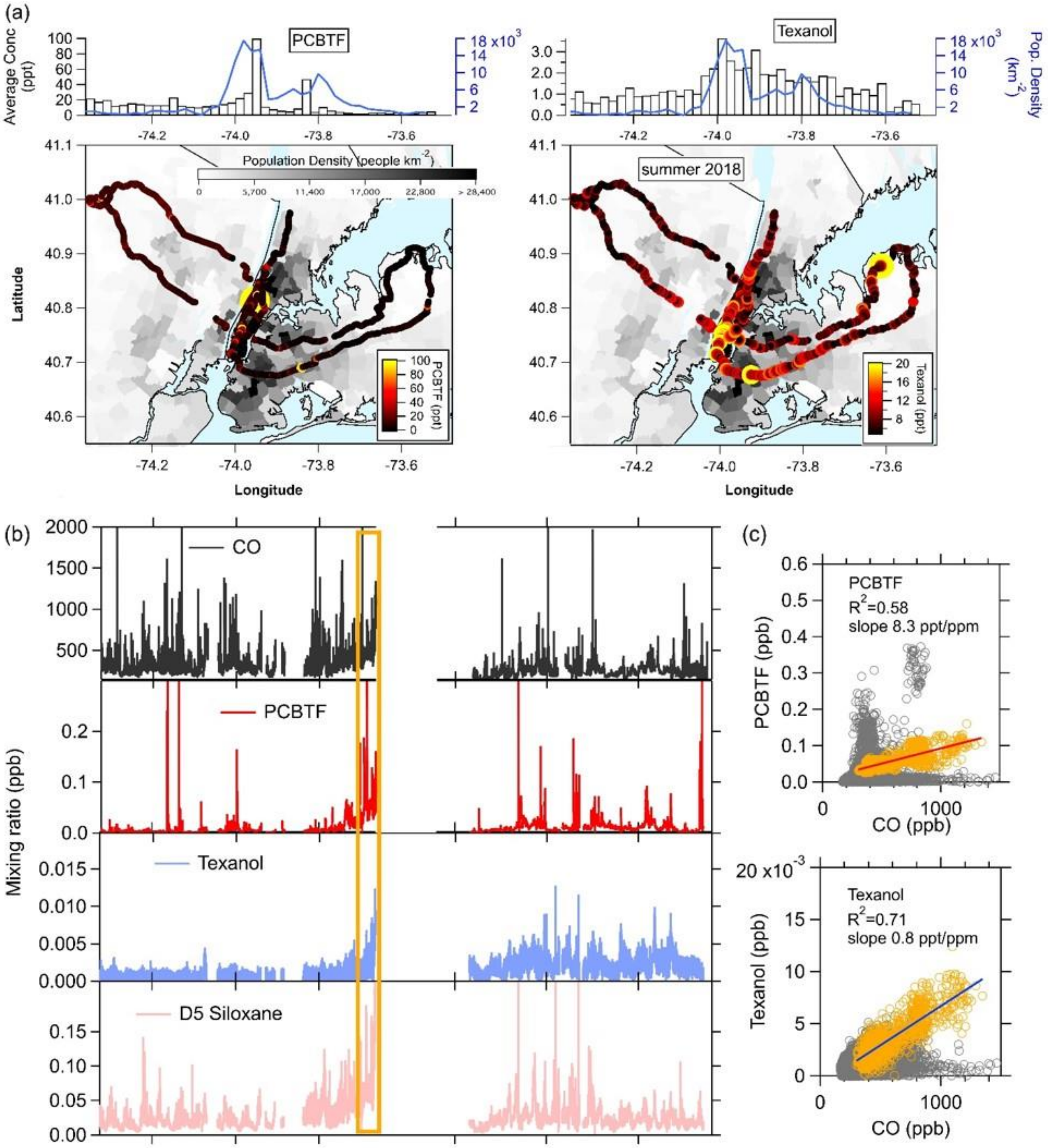
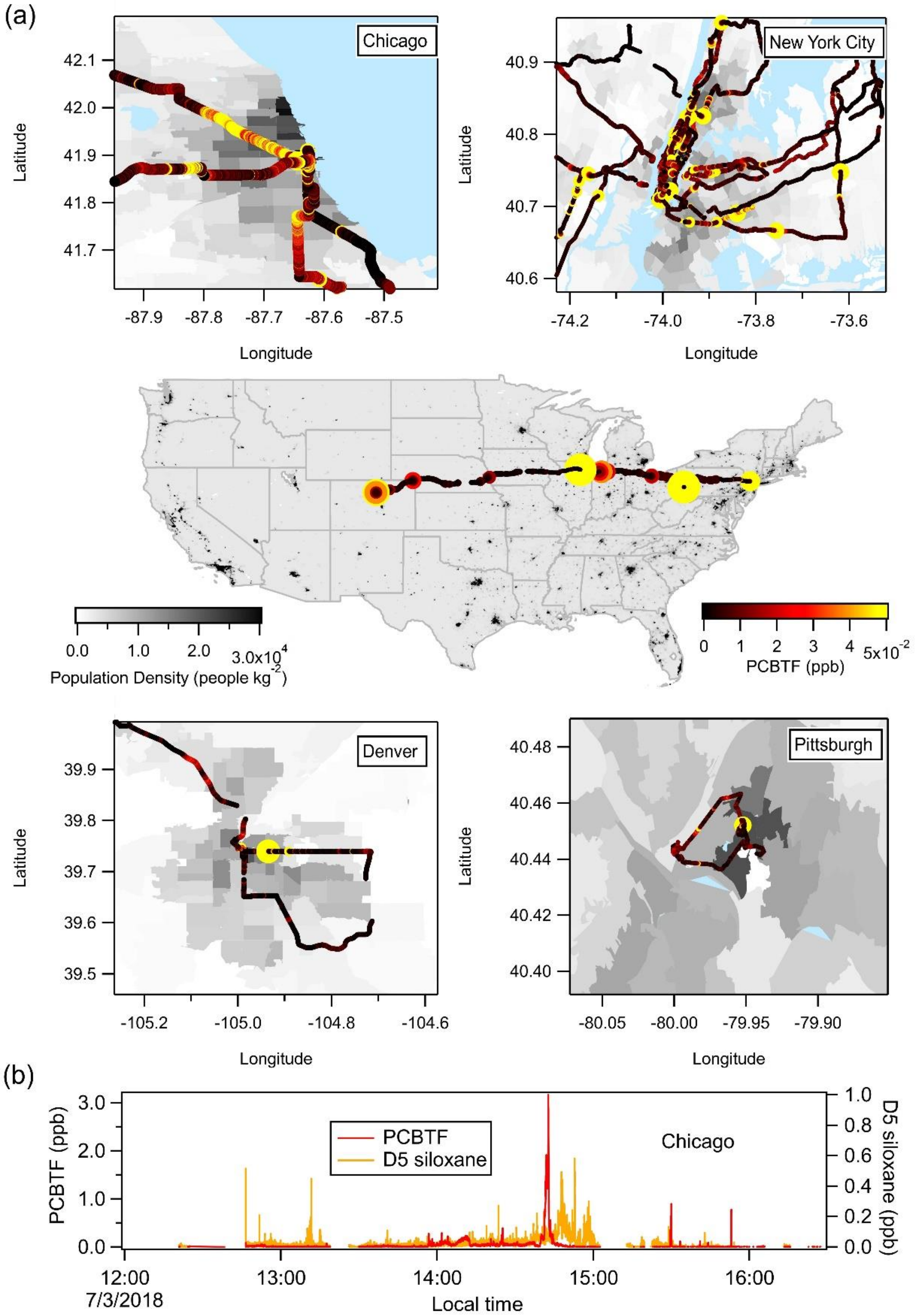


Figure 1: Summary of the PCBTF and Texanol measurements in New York City: (Map) Color-coded NOAA Mobile Laboratory drive track on a map of the population density. (a) Binned population density and mixing ratios. (b) Time series of CO, PCBTF, Texanol, and D5 siloxane for winter and summer months. The 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).


(a)
Chicago
Latitude
42.1
42.0
41.9
41.8
41.7
-87.9
-87.8
-87.7
-87.6
-87.5
Longitude
New York City
Latitude
40.9
40.8
40.7
40.6
-74.2
-74.0
-73.8
-73.6
Longitude
0.0
1.0
2.0
3.0x10^4
Population Density (people kg^-2)
0
1
2
3
4
5x10^-2
PCBTF (ppb)
Denver
Latitude
39.9
39.8
39.7
39.6
39.5
-105.2
-105.0
-104.8
-104.6
Longitude
Pittsburgh
Latitude
40.48
40.46
40.44
40.42
40.40
-80.05
-80.00
-79.95
-79.90
Longitude
(b)
PCBTF (ppb)
3.0
2.0
1.0
0.0
PCBTF
D5 siloxane
Chicago
D5 siloxane (ppb)
1.0
0.8
0.6
0.4
0.2
0.0
12:00
7/3/2018
13:00
14:00
15:00
16:00
Local time

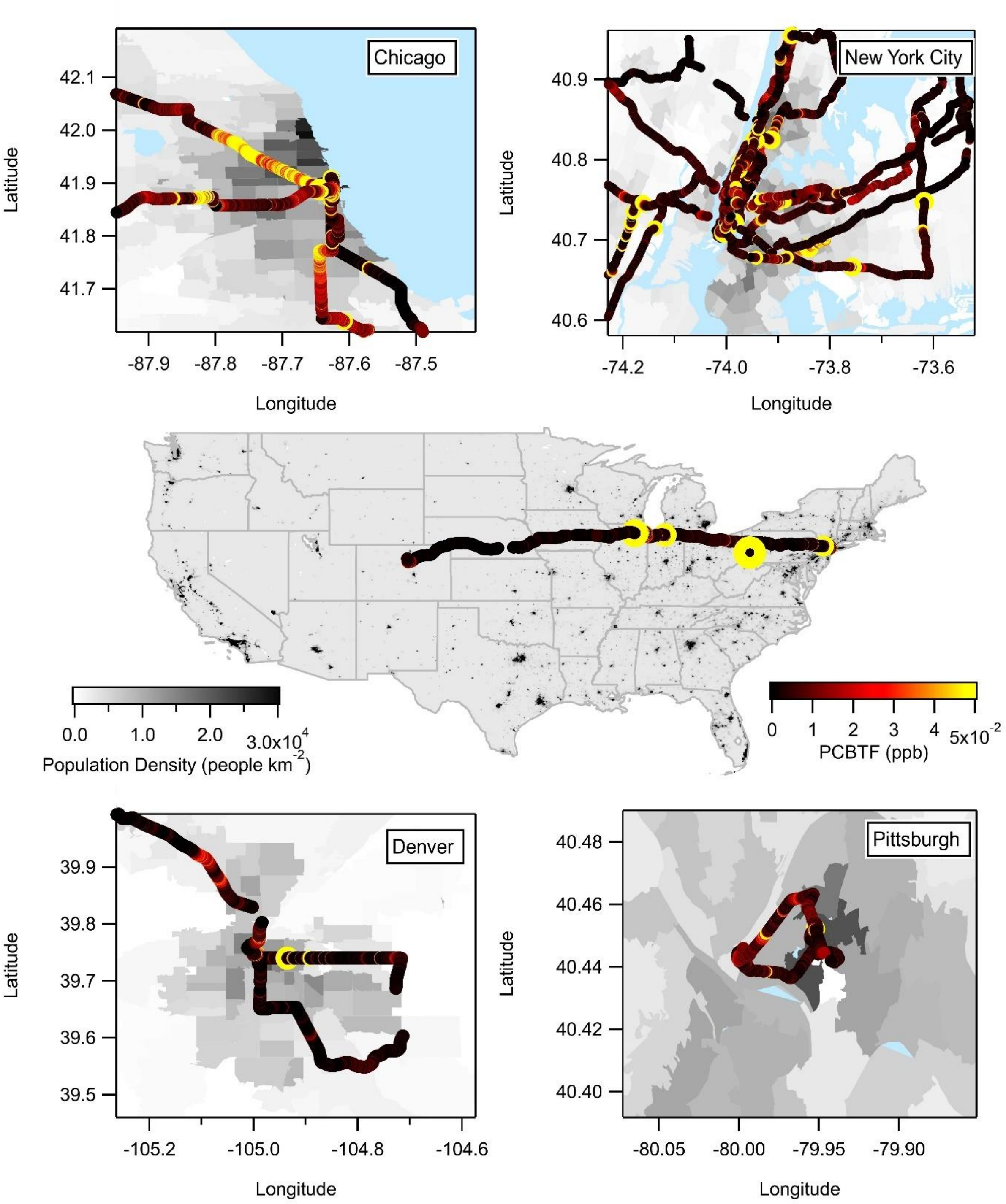
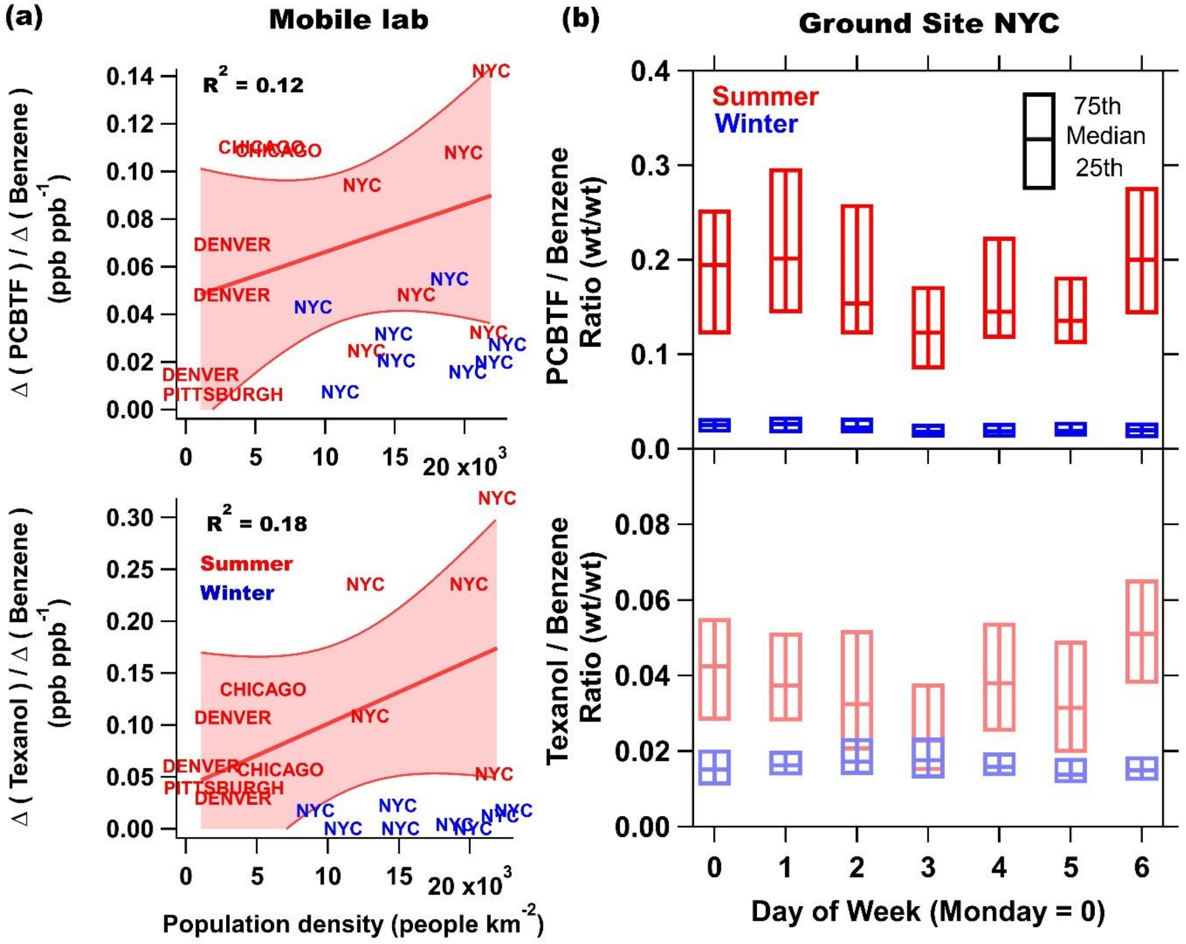


Figure 2: **~~(a)~~ Summary of the PCBTF ~~and Texanol~~ measurements from Chicago, New York City, Denver, ~~and~~ Pittsburgh, and the transition drives between the cities. ~~(b) Time series of PCBTF and D5 siloxane during Chicago drives.~~**


(a)
Mobile lab
(b)
Ground Site NYC
R² = 0.12
R² = 0.18
Δ (PCBTF) / Δ (Benzene) (ppb ppb⁻¹)
Δ (Texanol) / Δ (Benzene) (ppb ppb⁻¹)
Population density (people km⁻²)
0
5
10
15
20 x10³
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.05
0.15
0.20
0.25
0.30
NYC
CHICAGO
DENVER
PITTSBURGH
Summer
Winter
75th
Median
25th
PCBTF / Benzene Ratio (wt/wt)
Texanol / Benzene Ratio (wt/wt)
0.0
0.1
0.2
0.3
0.4
0.00
0.02
0.04
0.06
0.08
Day of Week (Monday = 0)
0
1
2
3
4
5
6

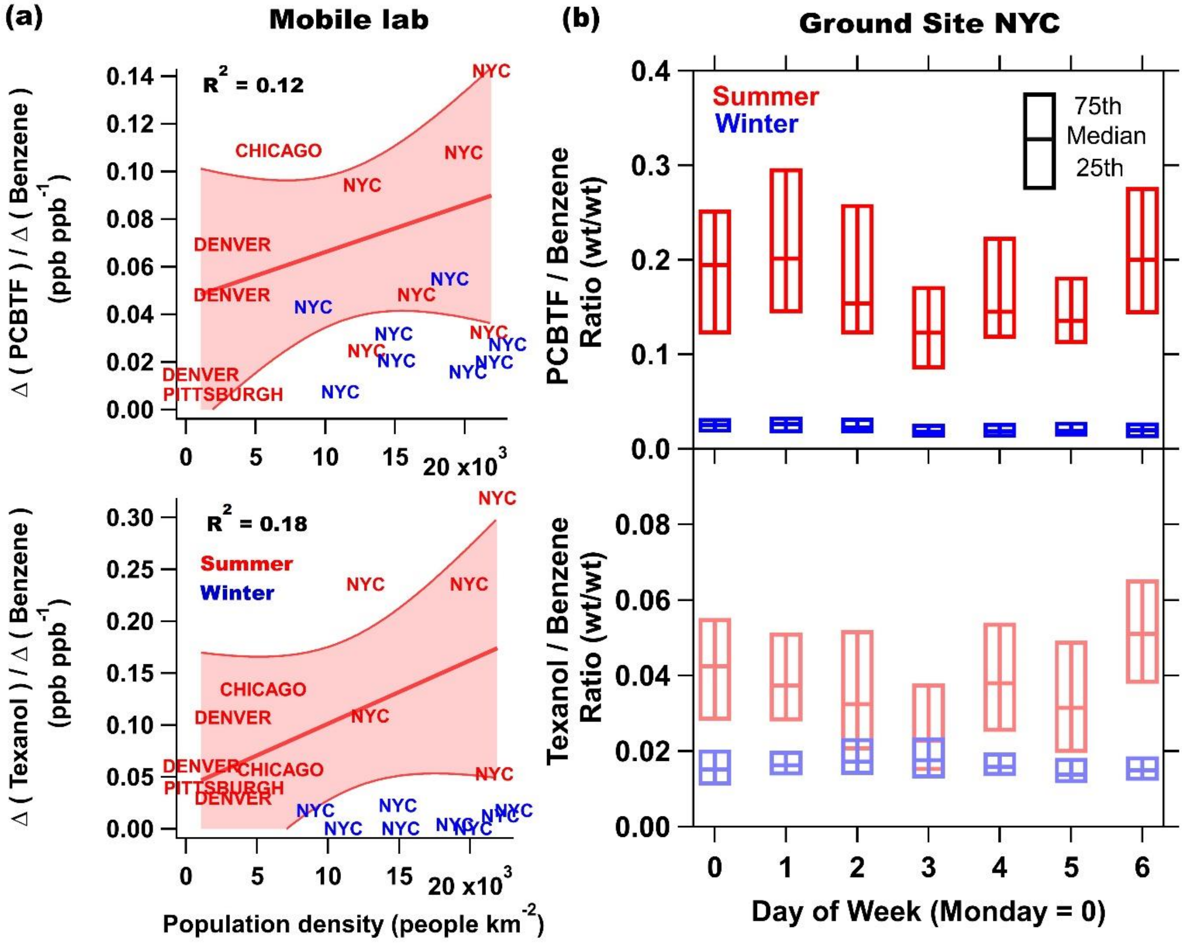
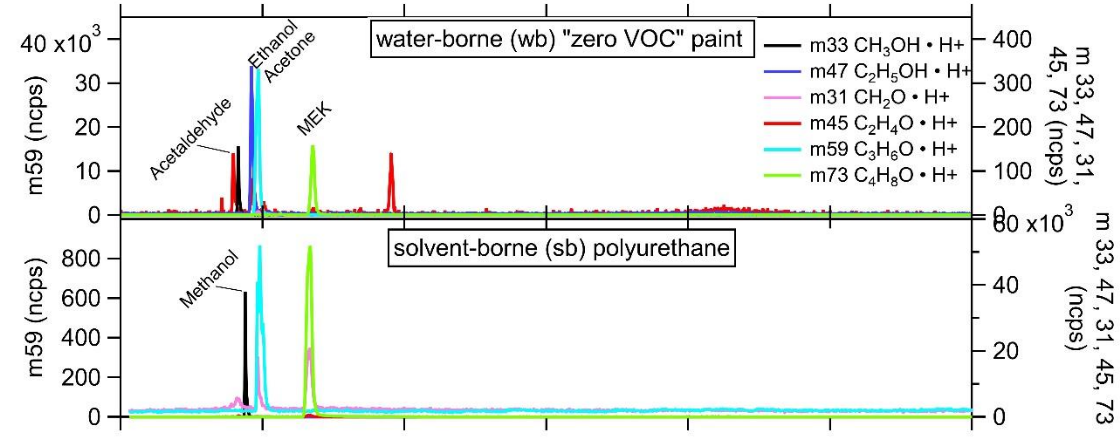
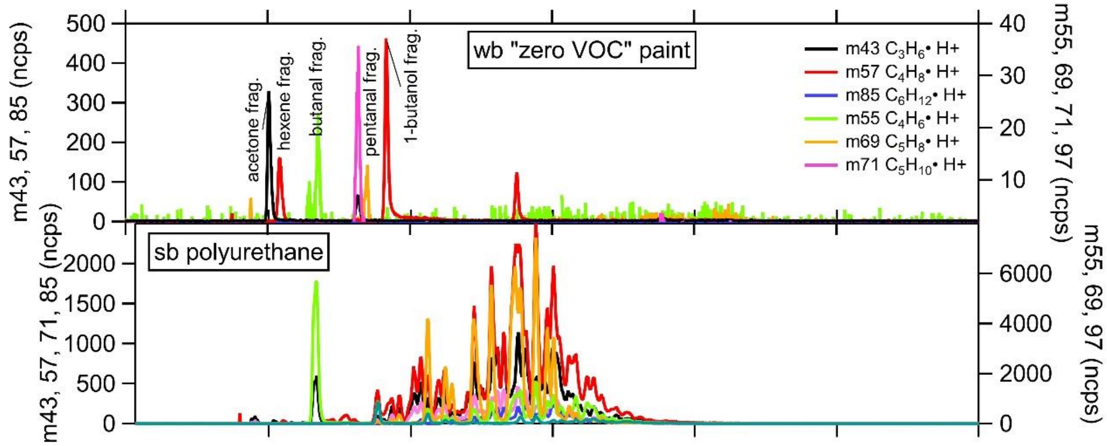


Figure 3: (a) The enhancement of PCBTF and Texanol relative to the enhancement of benzene versus the population density in summer (red) and winter (blue) in various cities. Enhancements were calculated by subtracting the background median taken from measurements upwind of cities with the lowest mixing 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.

(a) Oxygenates



(b) Hydrocarbons



(c) Aromatics

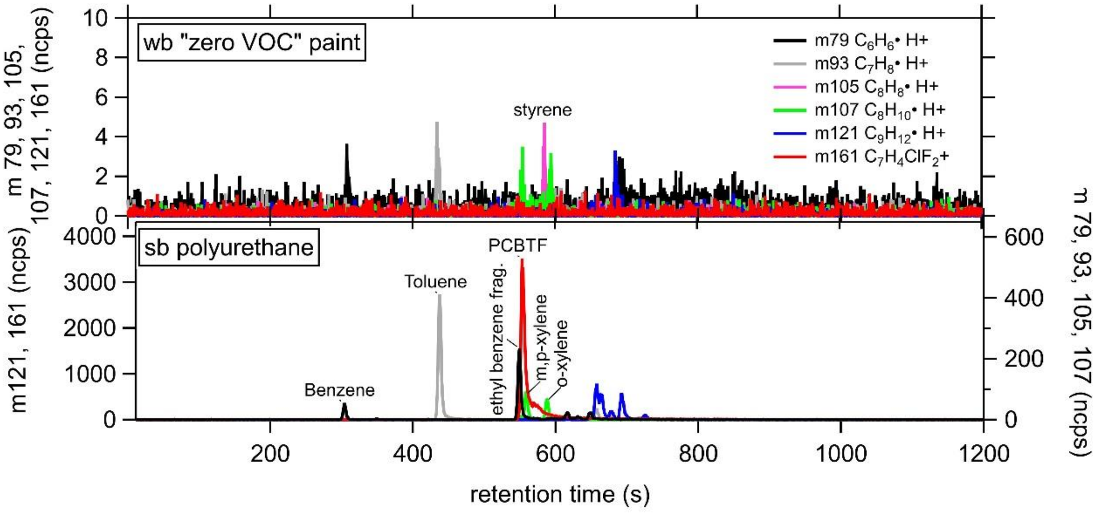
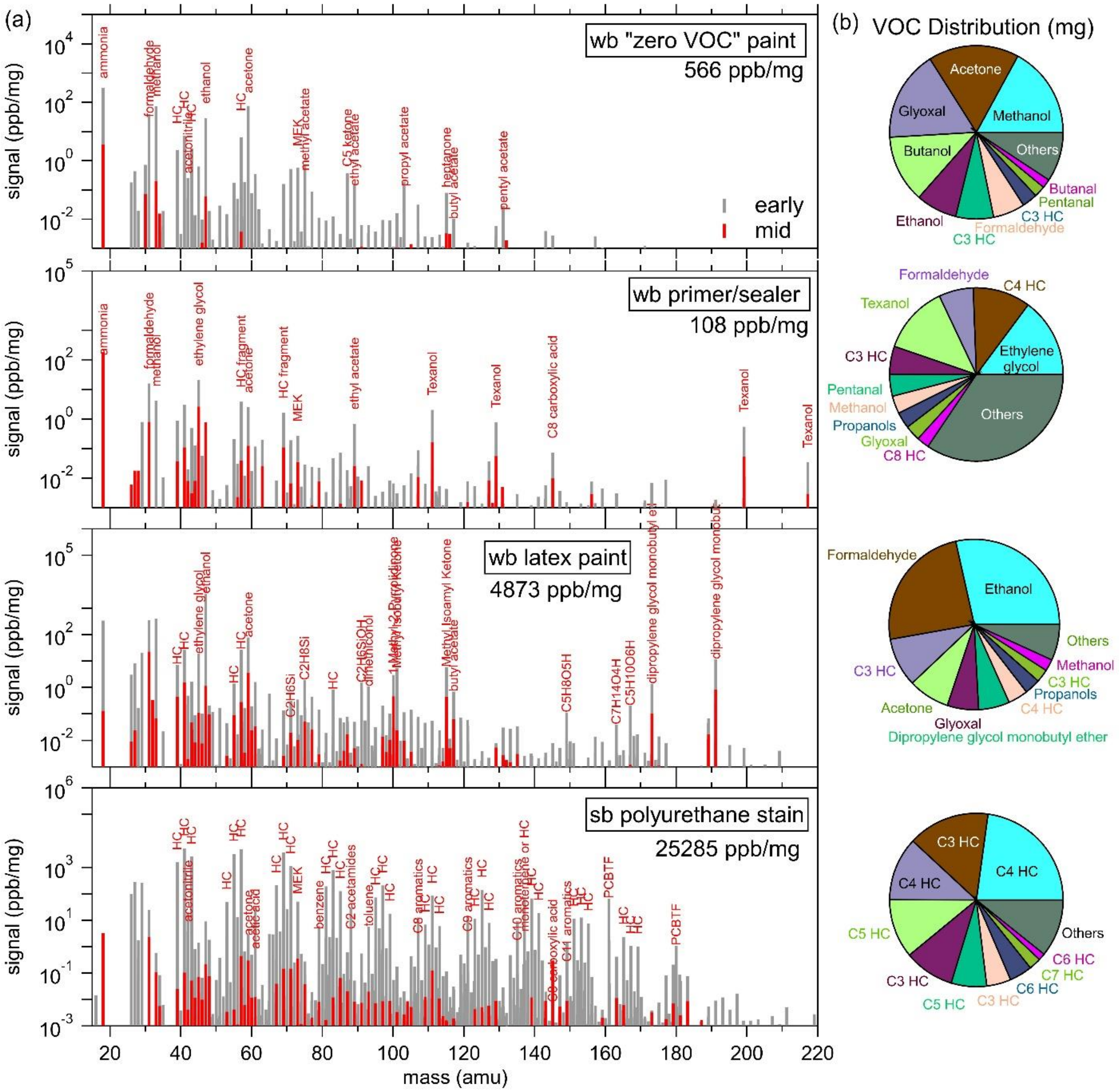


Figure 4: GC-PTR-ToF chromatogram from the headspace of a water-borne (wb), "zero VOC" low odor paint with ink and a solvent-borne (sb) polyurethane stain for (a) small oxygenates, (b) hydrocarbons, and (c) aromatics.


(a)
(b) VOC Distribution (mg)
wb "zero VOC" paint
566 ppb/mg
wb primer/sealer
108 ppb/mg
wb latex paint
4873 ppb/mg
sb polyurethane stain
25285 ppb/mg
signal (ppb/mg)
mass (amu)
early
mid
ammonia
formaldehyde
methanol
ethanol
acetone
acetonitrile
HC
MEK
methyl acetate
C5 ketone
ethyl acetate
propyl acetate
heptanone
butyl acetate
pentyl acetate
ethylene glycol
HC fragment
Texanol
C8 carboxylic acid
C2H6Si
C2H8Si
C2H6SiOH
dimethicone
Methyl Isoamyl Ketone
C5H8O5H
C7H14O4H
C5H10O6H
dipropylene glycol monobutyl ether
acetic acid
benzene
C2 acetamides
toluene
C8 aromatics
C9 aromatics
C10 aromatics
monoterpene or HC
C9 carboxylic acid
C11 aromatics
PCBTF
Acetone
Methanol
Glyoxal
Butanol
Others
Butanal
Pentanal
C3 HC
Formaldehyde
Ethanol
C4 HC
Texanol
Ethylene glycol
Pentanal
Propanols
C8 HC
Dipropylene glycol monobutyl ether
C4 HC
C5 HC
C6 HC
C7 HC
10^4
10^2
10^0
10^-2
10^5
10^6
10^3
10^1
10^-1
10^-3
20
40
60
80
100
120
140
160
180
200
220

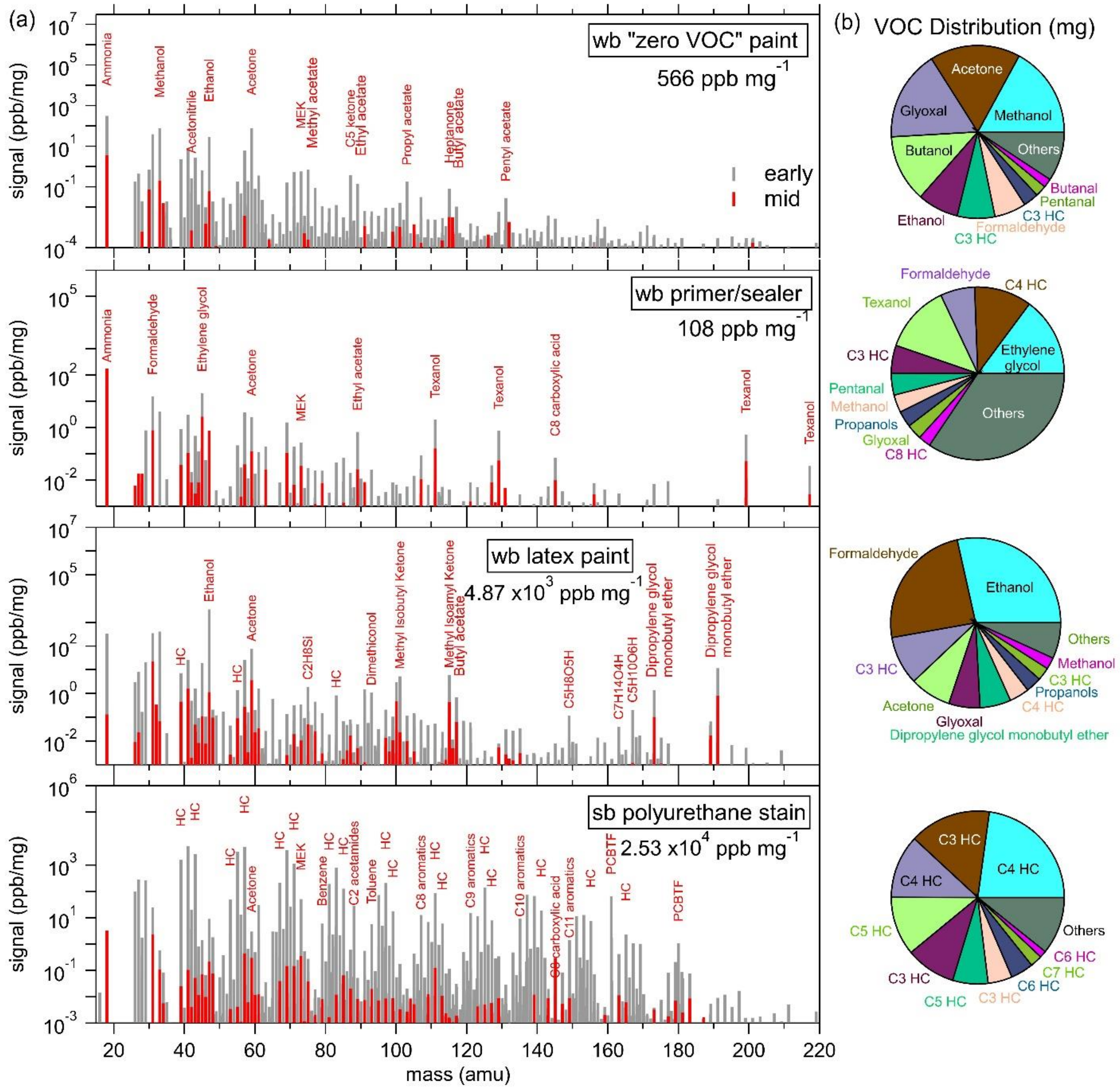


Figure 5: (a) PTR-ToF-MS mass spectra of a water-borne (wb) low VOC paint, a wb primer/sealer paint, a wb latex paint, and a solvent-borne (sb) polyurethane stain, where the major peaks are labeled by their most likely identification. The values in ppbv are normalized to the weight loss of the product 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.

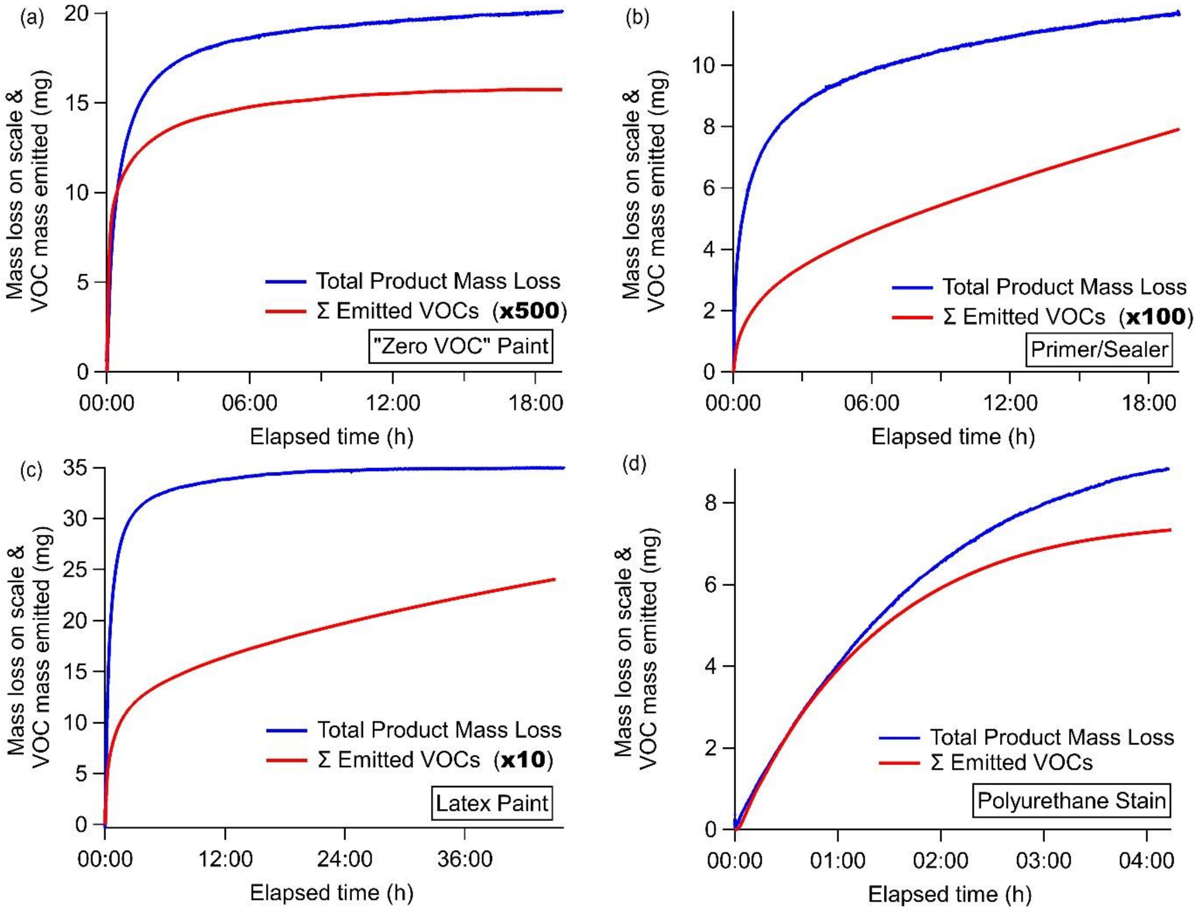


Figure 6: Total product mass loss measured on the scale (blue) overlaid with the total mass emitted as VOCs (red) measured by the PTR-ToF-MS as a function of elapsed time. The emitted VOC scalar is indicated in the legends.

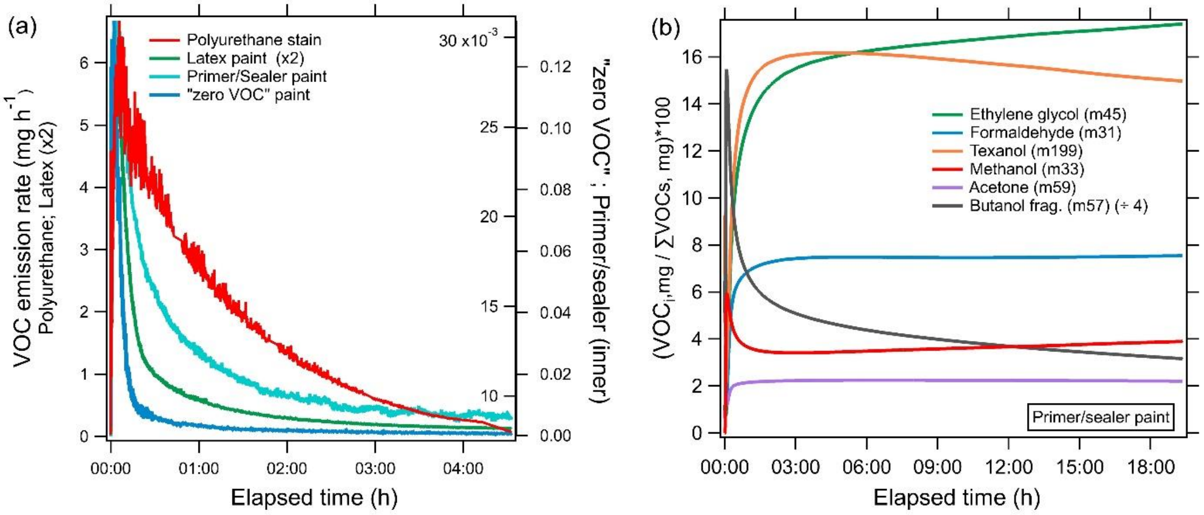


Figure 7: (a) Emission rates (mg h^{-1}) of all measured VOCs summed during evaporation experiments of different coating types: polyurethane stain (red), latex paint (green), primer/sealer paint (cyan), “zero VOC” paint (blue). (b) Time series showing the percent of integrated mass emitted as an individual 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.

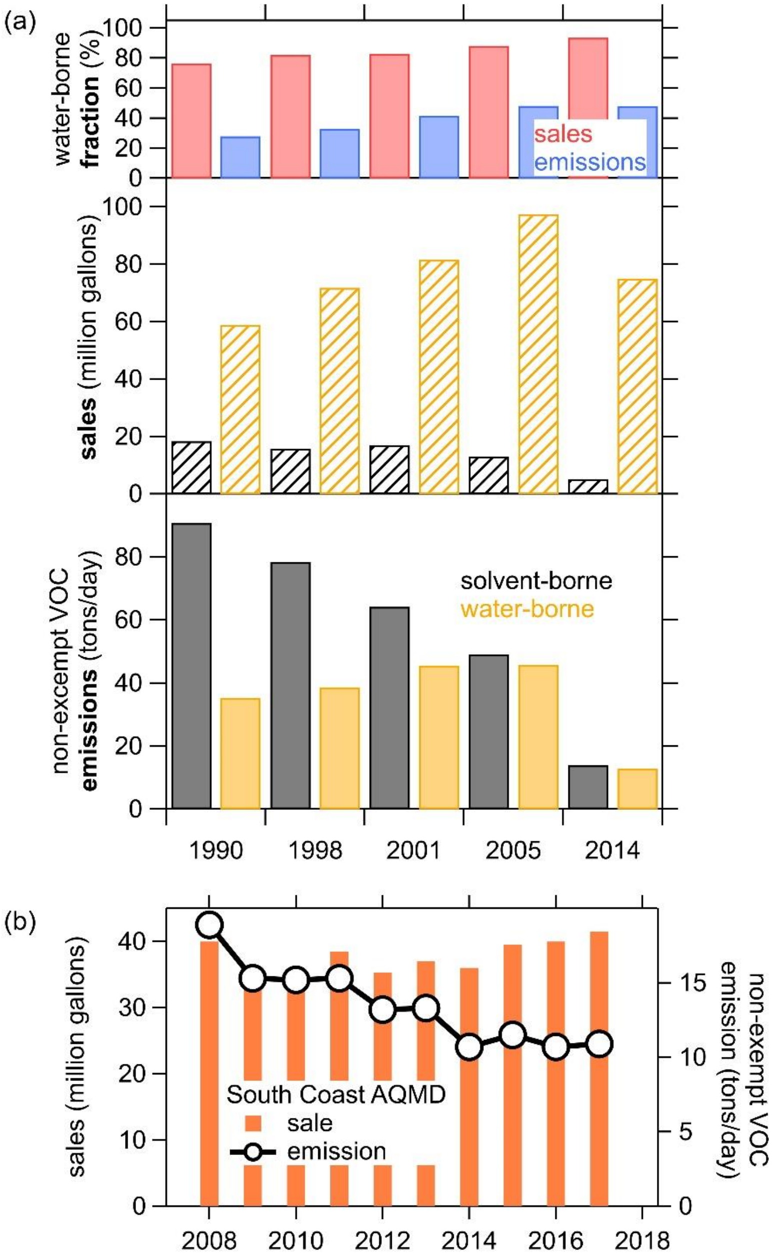


Figure 8: (a) Trends in paints and coatings sales and VOC emissions from the CARB coating surveys since 1990. (b) South Coast AQMD trend of coatings reproduced from: http://www.aqmd.gov/home/rules-compliance/compliance/vocs/architectural-coatings

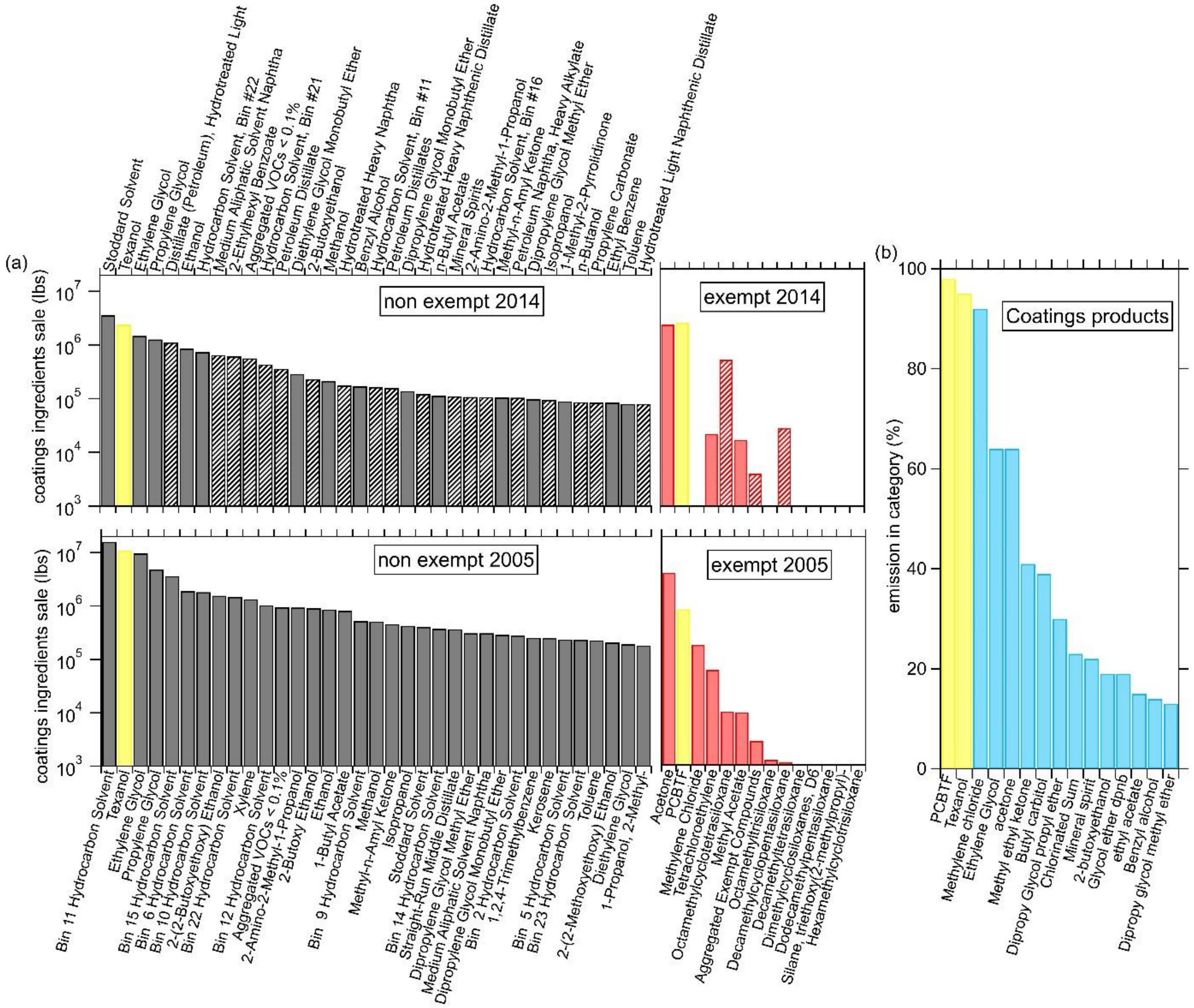


Figure 9: (a) The sale of top 35 non-exempt and the exempt VOC ingredients for coatings in 2005 and 2014 in California together with the (b) fraction of emissions in the coatings category of the 15 highest VOCs as determined by the FIVE-VCP inventory calculated using the method of McDonald et al. (2018a).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

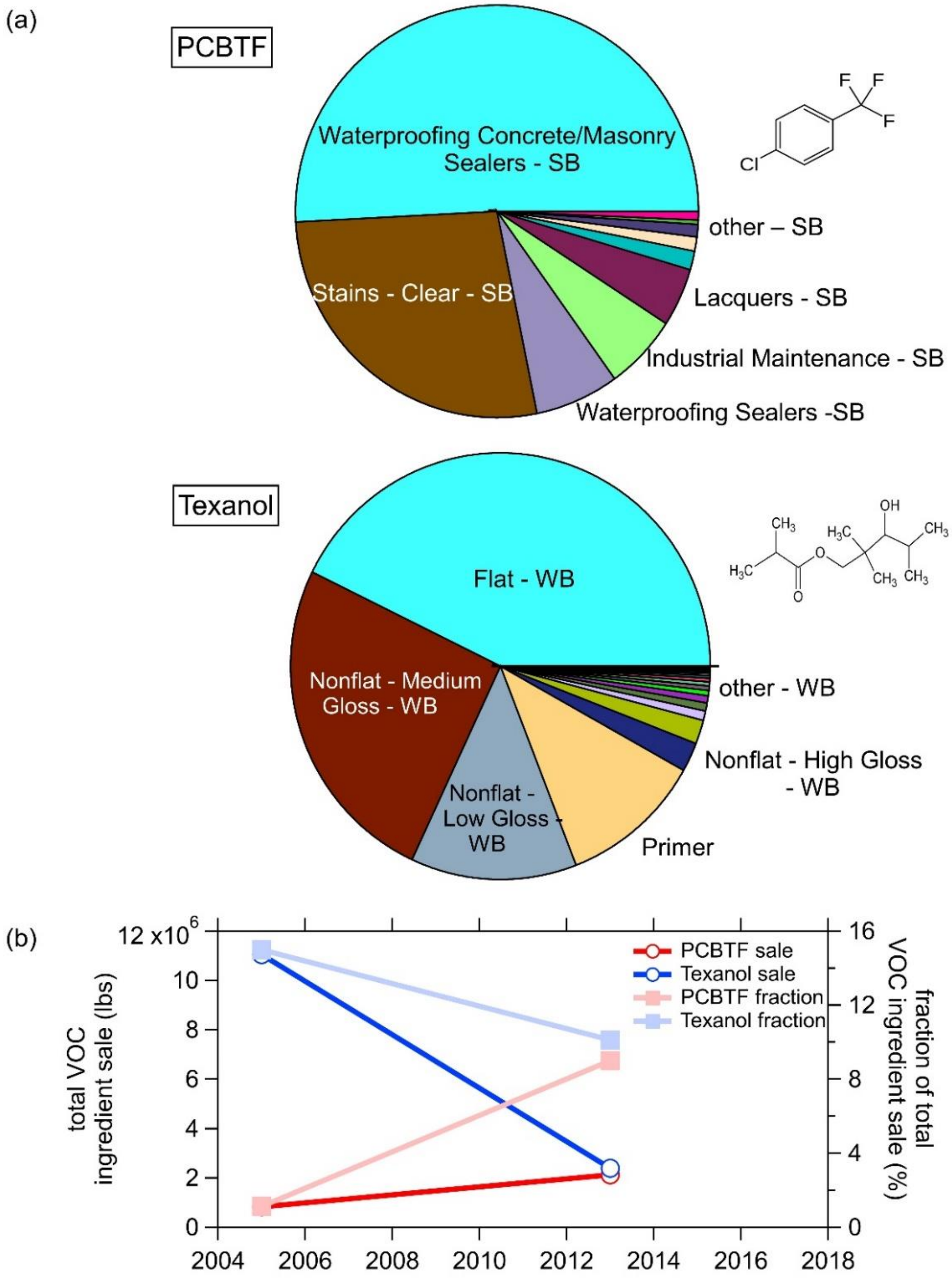


Figure 10: (a) PCBTF and Texanol use in solvent-borne (SB) and water-borne (WB) product categories in California and their (b) trends in sales and emissions.

S1. Detailed Description of GC Front End to PTR-ToF-MS

During operation, ambient air or headspace samples are sampled by the GC at a flow rate of 20 sccm through a 1.58 mm PTFE sample line into a heated 10-port 2-way chromatography valve (VICI) in the "load" position, as shown in Figure S1. The sample is then directed through a water trap to remove excess water and a sample trap to pre-concentrate sample analytes as described in detail below. The flow rate (20 sccm) is maintained by a mass flow controller (MFC2 in Fig. S1) and vacuum pump. After a user-specified volume has been collected (20-200 ml), the 10-port valve is switched to the "inject" position, and the sample and water traps are heated. Nitrogen (N_2) is used as a carrier gas to transport the VOCs to the head of the GC column (Agilent Technologies, 30 m, 0.25 mm ID, 1.4 µm film thickness) because N_2 does not significantly change the ion mobility in the PTR drift tube, unlike the lighter gases typically used in GCs (e.g., helium or hydrogen).

The water trap consists of 0.8 mm ID (1.58 mm OD) PTFE tubing inside a 15 cm length (1.5 cm OD, 1 cm ID) brass annulus that has a 2 mm fin that extends from the bottom of the tube into a 10 L liquid nitrogen dewar. This fin provides the cooling to the surrounding trap. The water trap temperature is maintained at -5°C during trapping using a ~250 W heater constructed of insulated Nichrome resistance wire wrapped around an outer stainless steel tube (3.2 mm OD, 2.5 mm ID) that holds the PTFE. A 1/16" type-T thermocouple probe is mounted between the stainless steel and PTFE tubing to measure and control the cold and warm (trapping/releasing) temperatures. After the sample is injected, the water trap is heated to 50°C and nitrogen pushes water vapor out through a vent port in preparation for the next sample. This purge flow rate is ~ 10~~2~~0 ~~sccm~~ mL min^{-1} and controlled by a flow restrictor. There are some losses of the heavier (~C8 and larger) VOCs within the water trap, but because the temperatures are controlled and consistent, these losses are accounted for during calibration.

The sample trap is a 17 cm piece of 0.32 mm ID passivated stainless steel guard column (Restek Corporation) suspended inside a piece of thin-walled hypodermic stainless steel tubing (1.59 mm OD, 1.43 mm ID). The gas fittings on either end are modified 1/32" chromatography fittings designed to fit inside small brass "end heaters". The purpose of these end heaters is to prevent VOCs from being trapped outside of the intended cold zone. The sample trap and stainless steel hypodermic tubing are electrically isolated from the rest of the assembly by using PTFE transfer lines and vespel (VICI) ferrules. The sample trap is suspended inside a piece of copper in the shape of a thin-annulus similar to the brass one described above. A 5 mm thick copper fin (15 cm long) is connected to the bottom of the copper annulus and extends into the same liquid nitrogen to provide cooling. The sample and water traps are mounted above the dewar and insulated using tightly fitting polystyrene foam insulation. During the sample collection period, the sample trap is maintained at a user-defined set point (typically -100 °C) by running an AC current from a 120:3 V transformer directly through the thin-walled hypodermic tubing. A type T thermocouple is encapsulated between the trap itself and the hypodermic tubing to measure and control the temperature.

During sample injection, the sample trap is heated to 110°C and forward flushed with N_2 carrier gas that transfers the trapped analytes to the 10-port valve and then on to the GC column through a heated transfer line (40°C) at 8 sccm. At the same time, the water trap is flushed at 40°C with N_2 carrier gas at a flow of 100 mL min^{-1}. The GC oven starts at 40 °C and held for 2 minutes. The temperature is then ramped at 10 °C min^{-1} to 150 °C. It is held at the final temperature for 30 seconds before being cooled again in preparation for the next sample. The four-port valve is shown directing column effluent to the mass spectrometer, while ambient air is vented. Depending on the application, 1-5 minute samples can be collected and chromatogram lengths of 10-20 minutes can be chosen such that the total run time is between 15 and 30 minutes. LabVIEW (National Instruments) software controls the sequence of events, hot and cold trap temperatures, transfer line heaters valve switching, sample flow and carrier gas flow. Calibration standards containing components with carbon numbers ranging from acetone (C3) to monoterpenes (C10) were tested to ensure that compounds were trapped and released through the water trap, sample trap and sampling lines and could be quantitatively detected by the PTR-ToF-MS. Both polar and non-polar compounds were tested including acetone, isoprene, BTEX compounds, indene, crotonaldehyde, 2,3, methyl buten-2ol, and methyl ethyl ketone. To analyze larger (and less volatile) molecules such as C12-C15 alkenes, sesquiterpenes, tri-isopropyl benzene or Texanol (C12), the trapping system would have required modifications. Among these are higher transfer line temperatures, higher water trap temperature, longer sampling times, higher GC oven temperature and possibly a different analytical column. Since the initial characterization included identification and quantification of the vast majority of VOCs observed in ambient air with a total cycle time of approximately 15 minutes, the design criteria were met. Further efforts to analyze heavier or lighter compounds (e.g. acetylene) were not pursued.

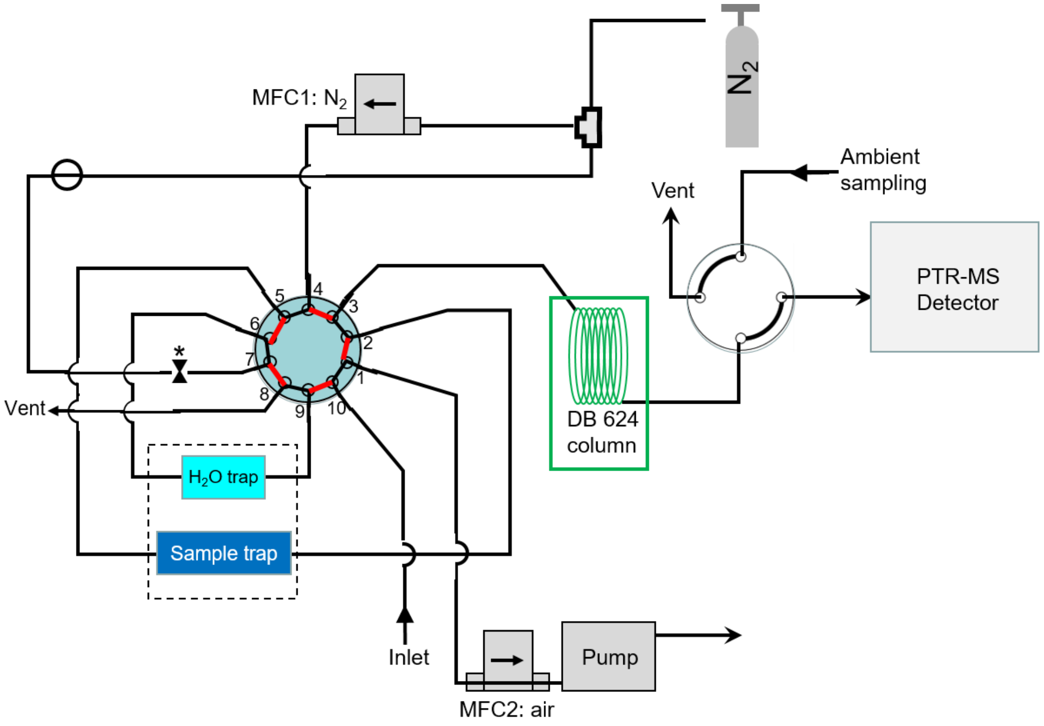


Figure S1. The GC front-end instrument diagram showing the load (red) and inject (black) positions of the 10-port 2-way chromatography valve.