

# ***Interactive comment on “Volatile organic compound emissions from solvent- and water-borne coatings: compositional differences and tracer compound identifications” by Chelsea E. Stockwell et al.***

## **Anonymous Referee #3**

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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

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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 < C<sub>14</sub>) that may be present in solvents-based coating products. The authors do lend a quick word to LVP-VOCs 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.

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.

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

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depleted of certain volatile constituents before sampling was conducted.

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?

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.

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?

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.

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.

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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.

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.

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.

Minor points:

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

-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.

-Line 392: increased “from”.

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

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-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.

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