

## ***Interactive comment on “BAERLIN2014 – stationary measurements and source apportionment at an urban background station in Berlin, Germany” by Erika von Schneidemesser et al.***

### **Anonymous Referee #2**

Received and published: 1 April 2018

The study reports on VOC and PM measurements made in Berlin during the BAERLIN2014 field campaign. A variety of instruments were used to make measurements of VOCs (Canisters, Cartridges, PTR-MS) and PM (filters, particle number, surface area). These measurements are of great value to the atmospheric chemistry community, and provide insights on air pollution in a major European city. The main finding is that biogenic emissions are significant contributors to ozone and PM in Berlin. This is clearly an important finding. However, I have some critiques that hopefully will strengthen the study's main conclusion. Also, at times the manuscript seems to be written as an

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overview paper of the campaign, which distracts from the analysis of field measurements. With revisions strengthening the robustness of VOC results, along with streamlining the manuscript to emphasize key results, I believe this paper has the potential to be published in Atmospheric Chemistry & Physics.

### General Comments

(1) For estimating OH reactivity, the results appear to be based only on VOC canister samples. Canisters could be missing key VOCs, especially oxygenated compounds, which may contribute significantly to OH reactivity. Karl et al. (2018) recently found a large flux of oxygenated VOC emissions in a European city, around half of the total VOC flux, including more highly oxidized OVOCs. The more oxidized OVOCs, which Karl et al. measured using a PTR-ToF-MS, are not on the list of compounds listed in Table S1. Therefore, this study likely presents an upper bound estimate of biogenic VOC emissions on OH reactivity, due to missing OVOCs. Discussing potential gaps in canister sampling systems in measuring VOCs and how it could affect results of this study is warranted.

Karl, T., et al. (2018). "Urban flux measurements reveal a large pool of oxygenated volatile organic compound emissions." *Proceedings of the National Academy of Sciences of the United States of America* 115(6): 1186-1191.

(2) Since the analysis appears to focus on canister samples for measurements of VOCs and in estimating of OH reactivity. It is not clear why measurements by cartridge samples (Section 2.2.2.) and PTR-MS (Section 2.2.3.) are included in the manuscript, other than to show that such measurements were made in BAERLIN2014. If these measurement systems are to be included, a more thorough evaluation of their VOC data is needed. By contrast, I found the PM instruments described to be well discussed and presented in the Results & Discussion section.

(3) Lines 452-467. The lack of agreement between the PTR-MS and VOC canister sampling analysis is disconcerting. While it is true that the PTR-MS may lack speci-

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ficity of individual compounds at a given  $m/z$ , some masses have been fairly well characterized now in urban air, including OVOCs (e.g., acetaldehyde, acetone, MEK, and methanol), aromatics (e.g., benzene and toluene), and monoterpenes (see Warneke et al., 2007). The way this paragraph is written, it appears to dismiss the PTR-MS measurements. However, there are also questions about sampling artifacts of key classes of compounds by canisters. For example, Lerner et al. (2017) report significant sampling artifacts present in canister samples of OVOCs and heavy aromatics (C9+). The analysis of VOC measurements could be strengthened by a more thorough evaluation for why differences are observed in the PTR-MS and canister samples, and by leveraging measurements from the two systems later in the analysis, rather than only highlighting results from the canister samples. The discussion mainly focuses on correlations, but are there any systematic biases in concentrations between the two instruments?

Warneke, C., et al. (2007). "Determination of urban volatile organic compound emission ratios and comparison with an emissions database." *Journal of Geophysical Research-Atmospheres* 112: D10S47.

Lerner, B. M., et al. (2017). "An improved, automated whole air sampler and gas chromatography mass spectrometry analysis system for volatile organic compounds in the atmosphere." *Atmospheric Measurement Techniques* 10(1): 291-313.

#### Specific Comments

(4) Line 165. It is not clear here how terpenes are affected by canister transport and storage.

(5) Line 435. It is not clear what the "BLUME network" is. Some description about what this measurement is would be helpful.

(6) Line 440. It is not clear which instrument is located at street-level. In the following discussion, it is implied that the PTR-MS is at street-level, but not explicitly.

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(7) Line 464. What is  $m/z$  9? This molecule would be smaller than carbon, so not a VOC.

(8) Line 499. There are several points below the 1:1, suggesting increases in mixing ratios. It would be interesting to highlight what these compounds are, and whether their lack of decrease/increase in concentration is consistent with the literature.

(9) Line 522. Why is limonene not included under the biogenic category when it is measured (Table S1)? Not including limonene might understate the biogenic contribution. It would also help to break down the OH reactivity between isoprene,  $\alpha$ -pinene, and  $\beta$ -pinene for the Neukolln and Altlandsberg sites. Some terpenes may be manmade and not biogenic (Derwent et al., 2007).

Derwent, R. G., et al. (2007). "Photochemical ozone creation potentials (POCPs) for different emission sources of organic compounds under European conditions estimated with a Master Chemical Mechanism." *Atmospheric Environment* 41(12): 2570-2579.

(10) Section 3.5.1. While I do not disagree with any of the statements made here, it was not clear by the end of the section what the new insights were. Also, this section could benefit from describing the bulk composition first across all samples, and provide better context for the back-trajectory analysis.

(11) Line 696 – 703. Are the diesel and gasoline vehicle contributions from POA only? If so, a caveat may be warranted here that secondary PM from gasoline and diesel vehicles are not included, which are potentially important sources of PM from transportation (see Gordon et al., 2014).

Gordon, T. D., et al. (2014). "Secondary organic aerosol formation exceeds primary particulate matter emissions for light-duty gasoline vehicles." *Atmospheric Chemistry and Physics* 14(9): 4661-4678.

Gordon, T. D., et al. (2014). "Secondary organic aerosol production from diesel vehi-

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cle exhaust: Impact of aftertreatment, fuel chemistry and driving cycle." Atmospheric Chemistry and Physics 14(9): 4643-4659.

(12) Line 709. It is not clear how high concentrations of inorganics support the finding of high amounts of SOA. Please describe in further detail.

(13) Line 750. While I do not dispute that biogenic VOCs are reactive and have an outsized contribution on OH reactivity, I believe caveats are needed here that missing VOCs not measured could affect the BVOC contributions presented here.

(14) Figure 6. It would be helpful to label which sites are traffic-dominated, urban background, and urban park under the name of each site.

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