

Interactive comment on “Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities” by R. E. Dunmore et al.

Anonymous Referee #2

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Dunmore et al. claim to have made comprehensive measurements of gas-phase organics in London in the summer and winter months and have analyzed those measurements to suggest that emissions from diesel fuel use account for a large fraction of the OH reactivity and ozone and SOA production in London. Their findings challenge the way emissions from diesel use are currently accounted.

The manuscript is well written with a good compilation of figures to describe the results and to make conclusions. While I have no concerns about the methods used to make the measurements, I am slightly concerned about the interpretation of those measurements as they apply to OH reactivity and production of ozone and SOA. I have flagged those concerns in the section below marked “Major Comments”. Further, I found that the manuscript was quite light on the methods used to analyze the data. For example,

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it is unclear how the ozone reactivity was calculated in Section 3.5 or how the emissions are calculated in Section 3.4. I am sure to recommend publication in ACP if the authors provide a detailed response to those comments and improve (through an explicit description) the Methods section detailing the methods used to analyze the data. However, at this point, I do not recommend publication of the manuscript.

Having said that, their work has implications for the use of similar techniques to measure high molecular weight emissions of gas-phase organics in laboratory and field settings and more importantly, assessing the importance of these organic compounds for urban air quality.

Major Comments

1. Assumption about the source and composition of emissions: It seems like the authors have assumed a priori, presumably based on the work of Gentner et al. (2012), that tailpipe emissions from diesel vehicles (and even gasoline vehicles) can only be composed of hydrocarbons present in the fuel. Accordingly, they have assumed that only these can contribute to OH reactivity, ozone and SOA production in the atmosphere. Work from the group at Carnegie Mellon University (CMU) (Gordon et al., 2014a,b; Jathar et al., 2014) has showed that unspeciated emissions (that include intermediate volatility organic compounds (Robinson et al., 2007) and possibly are oxygenated and/or incomplete products of combustion (Ensberg et al., 2013)) that are hard to measure using conventional techniques and are unaccounted for in emissions inventories could be very important for SOA production. It is likely that they are also important for ozone production and influence atmospheric OH reactivity. I would encourage the authors to think about the implications of the CMU work on the results/conclusions in this manuscript. Particularly, I wonder if the CMU work alters the source-resolved results (gasoline versus diesel) of this work.

2. Residual analysis; not absolute analysis: The VOCs measured in this work (especially in summer) are somewhat processed and hence the ozone reactivity and SOA

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potential assessed in Figures 3, 4, 6 and 7 represent the residual OH reactivity and the residual potential of the sources (e.g., gasoline, diesel, biogenics, etc) to form ozone and SOA. However, the authors seem to suggest otherwise. I would be willing to agree that the analysis holds for winter where very few of the VOCs will have reacted.

3. No atmospheric loss assumption: I am not sure I understand what the authors mean by the “no atmospheric loss” assumption to deduce the concentration of organics in the C14 to C22 range. The Gentner work develops distributions of organics that are primary in nature, i.e. unoxidized. In contrast, this work measures somewhat-processed organics and hence the distribution of organics will be very different mostly because the higher carbon number species will react faster than the lower carbon number species. Hence, if I have interpreted the authors correctly, I think the assumption about “no atmospheric loss” on Page 9550, line 22 is quite poor. With the current method, not only is the residual reactivity (of what is left in the atmosphere) estimated to be higher but also that sources with higher carbon number compound emissions (e.g., diesel) will appear relatively more important than sources with lower carbon number compound emissions (e.g., gasoline). I would encourage the authors to think about ways in which this artifact could be corrected. For instance, the data could be corrected based on the relative [anticipated] differences in reaction rate constants (may be as a function of carbon number). Let's say one emits equal parts of a C10 and C20. If a C20 reacts four times faster than a C10, then after a certain time, one should see four times less C20 than C10.

Minor Comments

1. Page 9542, line 8: I do not find that the measurement methods provide as comprehensive a speciation as Gentner et al. (2013) or some recent techniques developed by the groups of Allen Robinson (Zhao et al., 2014) and Robert Yokelson (Yokelson et al., 2013), to name a few. Hence, the claim of a comprehensive speciation does not seem warranted.

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2. Page 9544, line 19 and onwards: The authors talk about the relevance of gasoline and diesel on urban SOA production but fail to cite the relevant references. I would recommend a short summary of what has been found so far. For example, the work of Bahreini et al. (GRL, 2012), and Gentner et al. (2012).
3. Figure 2: Clearly, the font size on this figure is too small and needs to be increased for better viewability. Same comment applies to Figures 1, 5, 6 and 7 in supplementary material.
4. Figure 4: The bars can be thinned significantly to create a single column figure.
5. Page 9549-9550, Section 3.2: Could the authors comment about the uncertainty in their estimates (visualized in Figure 3) of OH reactivity based on the assumption of using a surrogate n-alkane to model OH reactivity? Further, it is unclear how the authors separate the estimates in Figure 3 into each source? They cite the work of Gentner et al. (2012) but in doing so are they assuming that emissions of gasoline and diesel are nothing but unburned hydrocarbons?
6. Page 9551, line 22: Remove semicolon after “Assuming that”.
7. Section 3.4: Page It is unclear what methods the authors have used to determine emissions of organics by carbon number based on the measurements. I would recommend that the authors describe the methodology in a “Methods” section.
8. Page 9553, line 1: typo - “hence these have are”.
9. Sections 3.5 and 3.6: I would like to see a description of the methods used to determine ozone potential in Figure 6 (did the authors use the box model of Bill Carter?) and the SOA potential in Figure 7 in a “Methods” section before discussion of the results in Sections 3.5 and 3.6.

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