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# ***Interactive comment on “Airborne determination of the temporo-spatial distribution of benzene, toluene, nitrogen oxides and ozone in the boundary layer across Greater London, UK” by M. D Shaw et al.***

**M. D Shaw et al.**

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Received and published: 10 February 2015

1.1 From the introduction it seemed that one of the main objectives for this manuscript was to re-validate the National Atmospheric Emission Inventory (NAEI), which I think the authors did not do a good job in achieving this goal.

1.2 An objective of this manuscript was not to re-validate the NAEI. The aims of the manuscript are clearly stated as “(i) quantitatively determine the vertical, horizontal spatial and temporal distribution of VOCs, NO<sub>x</sub> and ozone mixing ratios across London

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from an airborne platform, with a view to identify dominant emission sources in the region using measured toluene to benzene (T/B) concentration ratios and (ii) wherever possible, compare these fast response airborne measurements with hourly ground-level measurements made by the national monitoring networks.” The NAEI was only mentioned within the introduction of the manuscript to put this work into a wider context.

1.3 In order to clarify our aims we have removed all mention of the NAEI in the manuscript as we agree its discussion within the context of this manuscript is confusing.

2.1 With the re-validation of the NAEI objective in mind, why did the authors only report benzene and toluene measurements? The PTR-MS is a powerful instrument that can measure a vast array of VOCs? Did the authors have in mind another manuscript to do so? It looks like it is a waste of money and resources for both the aircraft and ground site campaigns to report emissions of 2 aromatic compounds.

2.2/2.3 See response to NAEI above. The primary focus of this research project was to calculate highly spatially resolved (1km) VOC and NO<sub>x</sub> Eddy covariance fluxes across greater London from an airborne platform, only mixing ratio data is presented here. EC flux data will be made available in later publications. In order to obtain VOC mixing ratio data with a PTR-QMS suitable for virtually disjunct Eddy covariance flux calculation requires a minimum quadrupole ion dwell time of 0.2 secs per VOC at an acquisition rate of 2Hz. Hence only 2 compounds could be scanned for simultaneously. Benzene and Toluene were chosen as their emissions within urban regions are dominated by anthropogenic sources, and their ratios can be used to indicate the emission source type (eg vehicular, Industrial).

3.1 Pages 27340-27432, it looks like there was different measurement rates depending on the instrument, for instance GPS data were collected at 20Hz, NO<sub>x</sub> at 10 Hz, VOCs at 5 Hz, what did the author do to compare all their measurements is everything converted to 20 HZ to be able to compare with GPS data?

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3.2 GPS, VOC and NO<sub>x</sub> data were averaged to 1Hz in this work for comparison and analysis.

3.3 This is now made clear in the text. Pg 6 line 28 reads "In this work, the 10Hz data has been averaged to 1Hz, with detection limits for the 1Hz data were being ~75pptv for NO and 100pptv for NO<sub>2</sub> with approximate total errors at 1ppbv being 10 and 15% for NO and NO<sub>2</sub> respectively" Pg 8 line 2 reads "In this work, the 2Hz mixing ratios data has been averaged to 1Hz for analysis."

4.1 Also, in the NO<sub>x</sub> sampling section, the acquisition frequency was 10 Hz but why the detection limit is reported at 1 Hz? The VOC sampling was at 5 Hz why did the author use a repetition rate at 2 HZ?

4.2/4.3 NO<sub>x</sub> and VOC data was averaged to 1 Hz for analysis and comparison as we are only interested in ambient concentrations. Hence this is why the detection limits are both reported at 1Hz. This is now made clear in the text. The PTR-MS instrument conditions were chosen specifically to capture VOC data suitable for EC flux calculations, which will be the focus of later publications.

5.1 Page 27342, lines 11-12, the authors stated that they used a combination of stainless steel and Teflon tubing to minimize memory effect however on page 27343 lines 19-20 the author stated that the inlet was PFA? I think this caused some confusion so may be the authors can explain the setup better, which part of the inlet was made of Teflon and which part was made up of stainless steel?

5.2 The sample inlet was stainless steel, the sample line was Teflon.

5.3 Pg 8 lines 31-33 now read "During flights, ambient air was sampled from the forward facing stainless steel isokinetic inlet along a heated (70°C) 5 m  $\frac{1}{4}$ " Teflon tube (0.21" ID) pumped by a stainless steel diaphragm pump (Millipore) at a flow-rate of 22L min<sup>-1</sup>."

6.1 Page 27347, lines 4-6, the authors specify that "benzene, toluene and NO<sub>x</sub> shared anthropogenic sources with very few biogenics" how did the authors reach this conclu-

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sion and was it based on their measurements? How big is the influence of biogenic emissions on Greater London?

6.2 Benzene, Toluene and NO<sub>x</sub> direct emissions are the result of anthropogenic sources in urban regions. There is the potential for O<sub>3</sub> formation from biogenic VOC emission in London but this discussion is beyond the scope of this paper.

6.3 The text “benzene, toluene and NO<sub>x</sub> shared anthropogenic sources with very few biogenics” has been removed from the manuscript.

7.1 Page 27347, lines 5-10 on the time scale of the flights and in an area that is highly influenced by fresh vehicular emissions of toluene and benzene? How big of an influence is photochemical aging?

7.2 Photochemical aging of Toluene and Benzene in Greater London should be relatively small based upon their atmospheric lifetimes. Whilst NO/NO<sub>2</sub> ratio will be affected on these timescales the total NO<sub>x</sub> mixing ratio would be conserved. However, the measured Toluene/Benzene ratios in suburban London ranged between 1.1 – 1.3±0.3 ppbv ppbv<sup>-1</sup> compared to 1.8±0.5 ppbv ppbv<sup>-1</sup> (at 360m a.g.l.) observed within inner London which could be interpreted as increasing air mass age from emission and that sources of VOCs in suburban regions could be the product of local emission and horizontal advection from inner London (figure 3).

8.1 Page 27348, Lines 1-5, It looks that within experimental error there is no difference in T/B ratio between suburban and south-western London, it looks that both are coming from fresh emissions so why did the authors use photochemical aging to interpret their results?

8.2/8.3 There is a very clear trend in that the T/B ratio is highest in central London where traffic density is likely highest and steadily decreases as we moved away from this region. Refer to figure 3. For instance. T/B ratio over central London = 1.8 ± 0.5 ppbv ppbv<sup>-1</sup>. T/B ratio over south-western Greater London (lat 51.35 – 51.42°) =

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$1.3 \pm 0.4$  ppbv ppbv<sup>-1</sup>. T/B concentration ratios in suburban (lat 51.30 – 51.35°) =  $1.1 \pm 0.3$  ppbv ppbv<sup>-1</sup>. It is our opinion that one possible reason for this could be could be increasing air mass age from emission and suggests that the sources of benzene and toluene in outer London are likely the product of local emission and horizontal advection from inner London.

9.1 Page 27355, in the conclusion section the authors did not mention how well their measurements agree with NAEI

9.2 The objective of this manuscript was not to re-validate the NAEI. The aims of the manuscript are clearly stated as. “(i) quantitatively determine the vertical, horizontal spatial and temporal distribution of VOCs, NO<sub>x</sub> and ozone mixing ratios across London from an airborne platform, with a view to identify dominant emission sources in the region using measured toluene to benzene (T/B) concentration ratios and (ii) wherever possible, compare these fast response airborne measurements with hourly ground-level measurements made by the national monitoring networks.”

9.3 In order to clarify our aims we have removed all mention of the NAEI in the manuscript as we agree its discussion within the context of this manuscript is confusing.

10.1 Did the authors see more photochemical aging in the flights parallel to wind direction (were these considered to be transformation flights)?

10.2 This was not the focus of the research flights. The measurement of plume evolution should be carried out using perpendicular transects across the plume at increasing distances from the emission source (Hopkins et al., 2009). Flying continuously parallel to the wind direction (as in this study) can create anomalies in the data interpretation as it's difficult to know the width of the plume which can lead to the potential of sampling different point sources within other plumes.

10.3 As a result of this comment, and due to the comments of reviewer 1 we have

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removed flights 7-10 from this analysis.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 27335, 2014.

**ACPD**

14, C12076–C12081,  
2015

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