We would like to thank Reviewer 1 for taking the time to review our manuscript and for providing us with constructive comments and suggestions for its improvement. We will respond to each individual comment below.

RC: Reviewer comment
AR: Author response

RC: The introduction is very short and does not review the relevant literature in sufficient detail. For example the authors later discuss the impact of the break down of nocturnal boundary layer and it would be useful to explore this in more detail in the introduction. Also the authors rely heavily on the assumption that traffic emissions are the dominant source of VOCs – it would be useful to see whether this is true in other locations.

AR: We will expanded the introduction to discuss the major sources of VOCs within major conurbations, referring to the results of source apportionment studies from other cities. A recent review by Kansal (2009) has shown that within urban environments vehicle related emissions are the dominant source of most (but not all) VOCs, typically accounting for > 50% of the total.

Although we discuss the effect of the nocturnal boundary layer within our manuscript, we do so only to interpret our findings. As these findings were incidental to the original objectives of our study we do not think the effects of boundary layer dynamics warrant discussion within the introduction. We feel this could detract from the primary aims of the study which were to characterize the predominant source of VOC emissions in the city and compare our direct "top-down" style measurements against the "bottom-up" modeling approach adopted by the NAEI.

RC: It would be useful to have a section here which focuses on the mean surface air pollution conditions observed during the campaign. The authors also comment that surface measurements of at least some of the VOCs studied and CO are available. It would be helpful to provide annual data and data for October to establish the how typical the conditions observed were.

AR: We agree that it is important to put the results from our campaign, which only represent a "snapshot" of the annual VOC emissions, into context. We will add a section which analyses the concentration data (Benzene, toluene and ethylbenzene) from the U.K governments Automatic Urban and Rural Network air quality monitoring site located on Marylebone Road over the previous 4 years (2001 – 2005).

RC: The exact dates of the measurements are not provided; neither is a section on the typical meteorological conditions during the campaign and how they compare to the rest of the year. This is important as later the authors make strong temperature related arguments and use the data as the basis for modelling annual emissions. Thus there is a need to establish that meteorological conditions during the observation period were not

only typical for that time of year, but that they were representative of the annual condition.

AR: We thank the reviewer for pointing out our oversight. The exact dates of the VOC measurements will be added to the method section.

We did not include a section on the campaign meteorology as this is included within the special issue introductory paper (Dallosto'et al., 2009). We will change the text to direct readers to this paper and include a brief summary of the meteorology during REPARTEE-I. In addition, we will include an analysis of historical temperature data taken from the London Weather Centre between 2001-2006. Briefly, this analysis showed the average temperatures encountered during the REPARTEE-I campaign (12.2* ± 1.8 C) to be representative of the annual average (12 ± 6 C). However, comparison with long-term average temperature measurements from the U.K Met Office show the ambient temperature during REPARTEE I to be unseasonably warm for October (2.5 C warmer than the long term average).

*** In the discussion paper the average campaign temperature, 15.9 C, was taken from measurements made by the sonic anemometer. It subsequently emerged that these data were offset by approximately 4 C. We now use data from a Vaisala WXT-510 sensor which was located on the roof of the tower for the duration of the campaign. The corrected average temperature was 12.2 C and the revised manuscript will be updated accordingly.**

RC: In the calculation of the flux footprint only a very limited range of conditions were used. The authors do not comment on the grid to grid variability of the emissions estimates, but if this is significant it would be useful to use a wider set of conditions to determine the typical footprint. This is especially true for the night time period when the potential for a weakly developed convective nocturnal boundary layer may complicate the identification of source areas.

AR: In the revised manuscript we will calculate the flux footprint for a range of atmospheric conditions (convectively unstable, stable and neutral) as well as for the average campaign meteorological conditions. However, as discussed in the manuscript, current footprint models are not fully applicable to the urban environment and these footprint calculations are only indicative. This prevents us from carrying out a much more detailed analysis.
In Fig. 9 of the manuscript we show the NAEI emission estimate for our flux footprint. The error bars on these estimates show the standard deviation of the grid squares within the flux footprint and thus show their variability. Although we state this within the figure caption, in our revised manuscript we will make sure this is clearly stated within the main text.

RC: A brief comment on the emissions inventory data would also be useful to establish the methods used to create the inventory and determine the predominant sources for the region.

AR: We will expand section 3.5 to include a brief description of the methodology adopted by the U.K national atmospheric emission inventory. We will also include a reference to the UK national atmospheric emission inventory mapping methodology report (Bush et al., 2006), which provides a very detailed account of the source apportionment used within the inventory.

RC: P17306 line 18 The authors comment that the aromatic compounds show two peaks with the second larger peak occurring in the evening. The increased magnitude of the second peak for these compounds is not obvious from Fig 2.

AR: There was typically a 6% difference between the morning and afternoon peaks for the aromatic compounds. We accept that this is not an obvious observation from fig 2. Therefore we will rephrase this sentence to read "second, slightly larger peak…".

RC: P17307 The authors comment on the long term trends that methanol and toluene show in the data set. These are not provided for the reader, and not compared with other compounds. Reasons for these trends could also be usefully explored and supported by the appropriate data sets.

AR: In our analysis of the data, the long term trends in methanol mixing ratios were particular to that compound and did not correlate with the ambient air temperature. There was also no clear association with a particular wind sector. As these trends were not mirrored in our methanol flux measurements, our conclusion was that the source of these higher mixing ratios lay outside of our flux footprint (not necessarily the city).
In the case of toluene concentrations, we directly compared our measurements with concurrent measurements of benzene and discussed the changes in the ratio between the two compounds within the text.
In our revised manuscript we will change the text to make it clear that the longer term trends in methanol and toluene did not correlate with temperature, or any of the other compounds. In addition, we will show polar plots of VOC concentrations and fluxes. In the case of both toluene and methanol, the wind sector dependence of concentrations and fluxes differs which provides further evidence of emission sources being located beyond the reach of the flux footprint of our Tower.

RC: P17308 The authors discuss the comparison of their data with surface data, however typical diurnal cycles or scatter plots are not provided. The differences between these two data sources could usefully be explored in more detail, especially as the authors later go on to discuss the potential impact of the layering of the boundary layer at night and resulting decoupling of the two layers. If these processes are operating there should be evidence in the mean concentration data sets – notably the diurnal variation in

concentration ratio between the two levels and difference in the lag between morning and evening concentration peaks. The authors also argue that measurements at the tower height may be influenced by sources outside the city. This not supported by data but could be effectively explored by examining the relationship in mean daily concentration with wind direction or using back trajectory modelling.

AR: The reviewer makes a good point. But, as we point in our response to a later comment below, the concentration measurements at the tower are affected by both local emissions (transported vertically from within the flux footprint) and advected emissions from outside the flux footprint (which do not register as a flux) and also by chemical processing, whereas curbside measurements are heavily influenced by local sources (traffic emissions). Therefore a more useful comparison would be a comparison of the diurnal surface concentration profile against the diurnal flux profile measured at the tower.
Analysis of ground level benzene concentrations from the U.K governments Automatic Urban and Rural Network air quality monitoring site located on Marylebone Road show two peaks, the first occurring at 09:00 and the second at 18:00. The diurnal flux profile for benzene shows a broad concurrent evening peak (18:00), but the morning peak is delayed by approximately 1 hour (10:00), which we attribute to the effect of the stable nocturnal boundary layer and its morning break up. The surface mixing ratios data are available at www.airquality.co.uk .

RC: P17308 3.2 VOC fluxes: The authors comment that during some nights the site becomes decoupled from the street canyon activity. However no evidence is provided for this. Model data for the BLD presented in Fig 5 is not convincing as it indicates that the BLD is always above 200m. The details of the model used are not provided to the reader, including whether or not an urban parameterisation has been employed to correct nocturnal estimates of BLD. Further the authors comment that a limitation of the model is that the lowest level it resolves is 250m – thus little is known about conditions when this is likely to be below this value. As a consequence this model was not a suitable choice to support their analysis of the night-time conditions. The authors refer to Barlow et al 2009 as a source of data – perhaps a case study of observations would provide more convincing evidence. Further, there should be evidence of decoupling in the sensible heat flux data. If the authors can show a peak in the heat flux coincident with the peak in the pollutant fluxes this would support their argument more effectively.

AR: We recognize the reviewers concerns regarding our choice of model for boundary layer height predictions. In our revised manuscript we will use the model by Arya (1981) which clearly shows the Telecom tower to be above the boundary layer at certain times. Much stronger evidence of the boundary layer dynamics is provided in the LIDAR measurements made during the subsequent REPARTEE-II campaign which will be presented by Barlow et al. (2009. A comparison of these LIDAR measurements against the PBL estimates provided by the algorithm of Arya

(1981) showed good agreement, and allowed us to optomise the algorithm for this site.
We thank the reviewer for their suggestion of looking for a coincidental peak in the sensible heat flux. Analysis of the data confirms VOC and sensible heat fluxes to peak at similar times, thus adding further credence to our interpretation of the data. We will include a statement to this effect in the revised manuscript.

RC: As it currently stands the arguments for the decoupling of the nocturnal boundary are based on speculation, which although supported by pollutant flux data is not convincingly supported by mean pollutant concentrations. Why would you expect mean concentrations to start to increase so early if the layers are separated?

AR: We agree with the reviewer that without supporting and concurrent measurements of boundary layer height by Lidar, our arguments regarding the nocturnal boundary layer can only be based on speculation. However, contrary to reviewer 1, we believe that both pollutant flux and pollutant concentration data support our argument. As shown by the diurnal plots (and as pointed out by the reviewer), VOC mixing ratios start to increase very early, but VOC fluxes do not. If the measurement site was coupled to the surface layer at this time, a simultaneous increase in concentration and flux would be observed. In this case, as no flux is observed at this time, the early morning increase in VOC mixing ratio must come from advection of air from outside of the flux footprint and not from turbulent transport from within the flux footprint.
A lag between traffic counts and measured emission fluxes was observed for CO2, for which the sources are better understood (Helfter et al., 2009).

RC: P17310 lines 10-20 The authors comment that the differences in the diurnal flux cycles observed between the VOC may result from changes in the sources at a diurnal scale. Please support this statement with references and emissions inventory.

AR: Traffic counts taken from Marylebone Road during the REPARTEE I campaign show that the traffic composition changes throughout the day, one example being fewer heavy goods vehicles (HGV) in the evening relative to cars.
Unfortunately the U.K national atmospheric inventory can only provide annual estimates and is therefore unable to provide information at the diurnal scale. In contrast, the emission inventory for Mexico City has a much finer temporal resolution. In this inventory, changes in source mix at a diurnal scale are clearly evident. In particular, the relative contributions from combustion sources (road traffic) and evaporative sources (painting, cleaning, printing etc.) clearly vary over the course of the day. Comparisons between this inventory and direct flux measurements have shown excellent agreement and are discussed in more detail by Velasco et al. (2009).

RC: P17311 It would be useful to see the diurnal cycle of CO that is used for the ratio calculations.

AR: Phillips et al. (2009) present a detailed analysis of CO mixing ratios and fluxes measured during the REPARTEE-I campaign. This analysis includes diurnal profiles of both fluxes and concentrations. We will direct readers to this paper in our revised manuscript.

RC: P17312 The authors argue that VOC processing is limited at night due to the absence of sunlight and titration of O_3 by NO. This implies that the layer is connected to the surface at night counter to earlier arguments. Perhaps it would be useful to look at ozone concentrations as an indicator of the coupling of the surface layers with those above.

AR: This argument is made on the basis of VOC/CO emission ratios. Any coupling / de-coupling would act on both VOC and CO as these come from similar ground-level sources. Both fluxes are suppressed by de-coupling but they are not zero. This suppression of exchange also suppresses the supply of ozone to the urban boundary layer. This can be seen in the ground-based data for the month of October 2006 which clearly shows the removal of O3 during the night time with concentrations decreasing from midnight to reach a minimum at 7 am. Ozone concentrations begin to rise from about 9 am. We ascribe this to the depletion of ozone in a shallow nocturnal boundary layer by dry deposition and titration by NO. This is entirely consistent with the evidence for the formation of a shallow nocturnal boundary layer provided by Barlow et al. (2009), PBL modelling, and our interpretation of the flux and concentration measurements at 200 m showing venting from below beginning at about 9 am. The ozone concentration data are available at www.airquality.co.uk. We have added a comment to the manuscript to this effect.

RC: Comparison with emissions inventory: This section would be stronger with the inclusion of more details in the methodology to establish the how representative the data observed during the campaign are of annual conditions. See earlier suggestions.

AR: please see our response to point 2.

References

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